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Assessment of some heavy metals pollution in water, sediments and *Barbus xanthopterus* (Heckel, 1843) in Tigris River at Baghdad city

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By

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بِسْمِ اللهِ الرَّحْمنِ الرَّحِيمِ

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Summary

The present work evaluated the concentrations of cadmium, zinc and manganese in filtered water and the sediments of Tigris River. The same metals were measured in the tissues of muscles, intestine and gills of Ghattan fish that were collected from the study area. The study also identified the physical and chemical properties of the water.

The severity of pollution of river sediments with studied heavy metals were assessed by using sediment pollution indexes such as geo-accumulation index (I-geo), pollution load index (PLI), contamination factor (C_f), contamination degree (C_d), enrichment factor (EF), and potential ecological risk index (E^i_f).

Four sampling stations were selected to conduct the study in Tigris River in Baghdad city. The samples were taken from the study stations at once every two months from October of 2011 until August 2012.

The study results showed that the mean concentrations heavy metals (cadmium, zinc and manganese) were 0.004 ppm, 0.023 ppm and 0.007 ppm, respectively in filtered water. Concentrations of these metals in filtered water of Tigris River showed seasonal variations during the study period and they were within permissible limit for Iraqi standard specifications.

Whereas, the mean concentrations of cadmium, zinc and manganese in sediments were 1.38 ppm, 86 ppm and 231.4 ppm, respectively. Concentrations of these metals in sediments showed significant seasonal variations and they were significantly higher than their levels in the water.

In fish muscles tissues the mean concentrations of cadmium, zinc and manganese were 0.0043 ppm, 0.0023 ppm and 0.03 ppm, respectively. The average of cadmium, zinc and manganese in the intestinal tissue of fish were 0.01 ppm, 0.0023 ppm and 0.03 ppm, respectively. The average

concentrations of same heavy metals in gills were 0.0121 ppm, 0.0026 ppm and 0.089 ppm, respectively.

The results of the present study showed that the metal concentrations in tissues of muscles, intestine and gills were several times higher than water and lower than sediments. These findings were confirmed by value of bioaccumulation factor (BAF) and bio-sedimentation factor (BSF).

Physical and chemical properties of river water recorded several values ranged between 12-42^{0}C, 9-32^{0}C, 6.9-8.2, 400- 810 µs/cm, 220-450 mg/l, 5.65-10.97 mg/l, 450 - 844 mg/l, 200-550 mg/l for air and water temperature, pH, electrical conductivity, total dissolved solid, dissolved oxygen, total suspended solid and total hardness, respectively in study area.

Which related with assessment of sediments pollution by using the ecological indexes, the results of geo-accumulation index (I-geo) for studied heavy metals cleared that the studied stations were unpolluted with Zn and Mn, while moderately polluted with Cd except station one that recorded slightly polluted with it. The values of pollution load index (PLI) showed that both of the stations 1 and 2 were unpolluted with total studied metals, while station 3 and 4 were polluted with total studied metals.

The results of contamination factor (C_f) observed that all the stations recorded considerable contamination with Cd, while low contamination with Zn was observed in all stations except the station 4 that recorded moderate contamination with it, while the sediments recorded low contamination with Mn in all studied stations.

Based on results of degree of contamination (C_d) indicates that the station 1 and 2 showed low degree of pollution with studied metals, while other stations showed moderate pollution. In addition to this the enrichment factor results (EF) showed that all stations can be classified as moderate enrichment with Zn and significant enrichment with Cd for all stations except station 4 was recorded very high enrichment.

Depending on potential ecological risk index for studied heavy metals the Cd recorded relatively high degree from potential ecological risk in the station 1, 2 and 3, while the station 4 which recorded a very high degree from risk potential, whereas the values of same index showed that Zn is not a potentially risk for all studied stations.

Table of contents

No.	Title	Page
	Summary	I
	Table of contents	IV
	List of figures	9III
	List of tables	9
	List of appendices	XI
	List of acronyms	XII
	Chapter one	
	Introduction and literature review	
1.1	Introduction	1
1.2	Aims of the study	2
1.3	Literatures review	2
1.3.1	Heavy metals pollution world-wide problem	2
1.3.2	Heavy metals in water	4
1.3.3	Heavy metals in sediments	5
1.3.4	Heavy metals in fishes	7
1.3.5	Heavy metals in *Barbus xanthopterus*	9
1.3.6	Selected heavy metals for this study	14
1.3.6.1	Cadmium (Cd)	14
1.3.6.2	Zinc (Zn)	15
1.3.6.3	Manganese (Mn)	16
1.3.7	Assessment of heavy metals pollution in sediments	17
1.3.7.1	Geo-accumulation index (I-geo)	18
1.3.7.2	Pollution Load Index (PLI)	20
1.3.7.3	Contamination Factor (Cf) and Degree of Contamination (Cd)	21
1.3.7.4	Enrichment Factor (EF)	22
1.3.7.5	Potential ecological risk index	23

No.	Title	Page
1.3.8	Assessment of heavy metals pollution in fish	24
1.3.8.1	Bioaccumulation Factor (BAF)	24
	Chapter two	
	Materials and methods	
2.1	Description of the study area	26
2.2	Instruments and chemicals materials for this study	33
2.3	Field study	35
2.3.1	Sampling procedure	35
2.3.1.1	Water sampling	35
2.3.1.2	Sediments sampling	35
2.3.1.3	Fish sampling	35
2.3.1.4	Water samples for dissolved oxygen sampling	36
2.4	Laboratory studies	36
2.4.1	Heavy metals analyses	36
2.4.1.1	Extraction of heavy metals from filtered water	36
2.4.1.2	Extraction of heavy metals from sediments	37
2.4.1.3	Extraction of heavy metals from fish	38
2.4.2	Physical and chemical measurements	38
2.4.2.1	Dissolved Oxygen (DO)	38
2.4.2.2	Total Suspended Solid (TSS)	39
2.4.2.3	Total Hardness (TH)	39
2.4.3	Sediment analyses	40
2.4.3.1	Total Organic Carbon in Sediments (TOC)	40
2.4.3.2	Soil texture	40
2.5	Ecological indexes	42
2.5.1	Sediment pollution indexes	42

No.	Title	Page
2.5.1.1	Geo-accumulation Index (I-geo)	42
2.5.1.2	The Pollution Load Index (PLI)	42
2.5.1.3	Contamination Factor and Degree of Contamination	43
2.5.1.4	Enrichment Factor (EF)	44
2.5.1.5	Potential Ecological Risk Index (E^i_f)	45
2.5.2	Calculation of Bio-Concentration Factor (BCF) and Bio-Sedimentation Factor (BSF)	45
2.6	Blank solutions	46
2.7	Statistical analysis.	46
	Chapter three	
	Results and discussions	
3.1	Heavy metals	47
3.1.1	Heavy metals (cadmium, zinc and manganese) in filtered water of Tigris River	47
3.1.1.1	Cadmium (Cd)	48
3.1.1.2	Zinc (Zn)	53
3.1.1.3	Manganese (Mn)	55
3.1.2	Heavy metals in sediments of Tigris River	58
3.1.2.1	Cadmium (Cd)	58
3.1.2.2	Zinc (Zn)	62
3.1.2.3	Manganese (Mn)	63
3.1.3	Heavy metals in *Barbus xanthopterus* fish in Tigris River	66
3.1.3.1	Cadmium (Cd)	66
3.1.3.2	Zinc (Zn)	70
3.1.3.3	Manganese (Mn)	72
3.2	Environmental parameters in Tigris River	78

No.	Title	Page
3.2.1	Physical and chemical proprieties	78
3.2.1.1	Air and water temperature	78
3.2.1.2	Hydrogen ion concentration (pH)	83
3.2.1.3	Electrical conductivity (EC)	87
3.2.1.4	Total dissolved solids (TDS)	89
3.2.1.5	Dissolved oxygen (DO)	91
3.2.1.6	Total suspended solids (TSS)	94
3.2.1.7	Total hardness (TH)	95
3.2.2	Soil texture	98
3.2.3	Total organic carbon (TOC) in sediments	99
3.3	Ecological indices	100
3.3.1	Assessment of studied heavy metals pollution in Tigris River sediments	100
3.3.1.1	Geo-accumulation index (I-geo)	100
3.3.1.2	Pollution Load Index (PLI)	101
3.3.1.3	Contamination Factor (C_f) and Degree of Contamination (C_d)	102
3.3.1.4	Enrichment Factor (EF)	103
3.3.1.5	Potential Ecological Risk Index (E^i_f)	104
3.3.2	Assessment of heavy metals pollution in *Barbus xanthopterus* fish	106
3.3.2.1	Bio-accumulation Factor (BAF) and Bio- Sedimentation Factor (BSF)	106
	Conclusions and recommendations	
1	Conclusions	109
2	Recommendations	110
	References	111
	Appendices	139

List of figures

Figure	Title	Page
1	*Barbus xanthopterus* (Heckel, 1843)	13
2-a	Map of Tigris River in Baghdad city with stations of the study area.	28
2-b	Station 1.	29
2-c	Station 2.	30
2-d	Station 3.	31
2-e	Station 4.	32
3	Variation of dissolved cadmium during the study period	50
4	Variation of dissolved zinc during the study period	55
5	Variation of dissolved manganese during the study period	57
6	Variation of cadmium in sediments during the study period	59
7	Variation of zinc in sediments during the study period	63
8	Variation of manganese in sediments during the study period	64
9	Variation of cadmium in muscles of fish *B. xanthopterus* during the study period	67
10	Variation of cadmium in intestine of fish *B. xanthopterus* during the study period	68
11	Variation of cadmium in gills of fish *B. xanthopterus* during the study period	68
12	Variation of zinc in muscles of fish *B. xanthopterus* during the study period	71
13	Variation of zinc in intestine of fish *B. xanthopterus* during the study period	71
14	Variation of zinc in gills of fish *B. xanthopterus* during the study period	72
15	Variation of manganese in muscles of fish *B. xanthopterus* during the study period	73
16	Variation of manganese in intestine of fish *B. xanthopterus* during the study period	74

17	Variation of manganese in gills of fish *B. xanthopterus* during the study period	74
18	Variation of air temperature (°C) during the study period	81
19	Variation of water temperature values (°C) during the study period	81
20	Variation of pH values in Tigris River during the study period	86
21	Variation of electrical conductivity during the study period	89
22	Variation of total dissolved solids during the study period	91
23	Variation of dissolved oxygen during the study period	94
24	Variation of total suspend solids during the study period	95
25	Variation of total hardness during the study period	97
26	Variation of metal pollution index of heavy metals in sediments of Tigris River	102

List of tables

Table	Title	Page
1	Latitudes and longitudes of study stations in Tigris River within Baghdad city	27
2	A list of instruments that were used in field and lab work	33
3	A list of chemical materials that were used in lab work	34
4	The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in filtered water of four studied stations	50
5	Compared studied elements (Cd, Zn and Mn) in filtered water of Tigris River with local and international standards limits.	51
6	Compared studied elements (Cd, Zn and Mn) in filtered water of Tigris River with local and international studies	51
7	The concentrations (Mean±SD) of different heavy metals	60

	studied (Cd, Zn, and Mn) in the river sediments of four studied stations	
8	Compared studied elements (Cd, Zn and Mn) in sediments of Tigris River with international standards	60
9	Compared studied elements (Cd, Zn and Mn) in sediments of Tigris River with local and international studies	61
10	The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in muscles of fish (*B. xanthopterus*) that collected from studied stations	69
11	The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in intestine of fish (*B. xanthopterus*) that collected from studied stations	69
12	The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in gills of fish (*B. xanthopterus*) that collected from studied stations	70
13	Compared study elements (Cd, Zn, and Mn) of fish *B. xanthopterus* in Tigris River with the international Standards	76
14	Compared studied elements (Cd, Zn, and Mn) of fish *B. xanthopterus* in Tigris River with other local and international studies	77
15	The concentrations (Mean±SD) of different studied physical and chemical parameters in the river water of the four studied stations	82
16	The correlation coefficient among studied water parameters	83
17	The correlation between studied dissolved heavy metals and water parameters	87
18	Sediment texture at study stations of Tigris River during study period	98

19	Geo-accumulation index (average I-geo values) for studied heavy metals in sediments of Tigris River	101
20	Contamination factor (C_f), degree of contamination (C_d) and pollution load index (PLI) of sediment samples collected from Tigris River.	103
21	Enrichment factor of heavy metals collected from Tigris River.	104
22	Potential ecological risk index for heavy metals collected from Tigris River.	105
23	The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in muscles of *B. xanthopterus* fish during the study period	107
24	The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in intestine of *B. xanthopterus* fish during the study period	108
25	The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in gills of *B. xanthopterus* fish during the study period	108

List of appendices

Table No.		**Page**
1	The correlation among cadmium concentrations in water, sediments and fish (muscles, intestine and gills)	139
2	The correlation among zinc concentrations in water, sediments and fish (muscles, intestine and gills)	139
3	The correlation among manganese concentrations in water, sediments and fish (muscles, intestine and gills)	140

List of abbreviations

Name	Acronym
American Public Health Association	APHA
World Health Organization	WHO
International Agency for Research on Cancer	IARC
International Occupational Safety and Health Information Center	CIS
International Center for the Agriculture Researches	ICARDA
Food and Agriculture Organization	FAO
International Programmer on Chemical Safety	IPCS
Department of Water Affairs and Forestry	DWAF
Water Pollution Control Legislation	WPCL
United Nations Environmental Programme	UNEP
United States Environmental Protection Agency	USEPA
Environmental Protection Agency	EPA
National Oceanic and atmospheric Administration	NOAA
National Standards Management Department	NSMD
Federal Environment Protection Agency	FEPA
European Commission	EC
Water watch Australia Steering Committee	WASC
Water Corporation	WC
National Academy of Science	NAS
International Atomic Energy Agency	IAEA-407

Chapter one

Introduction and literatures review

1.1 Introduction

In recent years there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the aquatic systems (Tijani *et al.,* 2005). There are basically three reservoirs of metals in the aquatic environment: water, sediment and biota (Saha *et al.,* 2001). Sediments are important sinks for heavy metals and also play a significant role in the remobilization of contaminants in aquatic system under favorable conditions and interaction between water and sediments (Grosheva *et al.,* 2000). The analysis of river sediment is a useful method of studying environmental pollution with heavy metals (Batley, 1989).

In a river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities (Shriadah, 1999). Tigris River receives many pollutants especially heavy metals when it is passing through Baghdad city, due to many human activities and factories throw pollutants into the river without any real treatments.

The pollution indexes evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Farkas *et al*., 2007). Several numerical sediment quality indexes were recently developed to provide interpretative tools for assessing chemical pollution. The most used approaches are geo-accumulation index (I-geo), pollution load index and enrichment factor.

1.2 Aims of the study:

1. Sediments, water and Ghattan fish were taken from Tigris River, in order to identify the seasonal variations in concentrations of cadmium, zinc and manganese in Tigris River.
2. Measuring some physical and chemical characteristics of Tigris River water such as temperature, pH, electrical conductivity, total dissolved solid, dissolved oxygen, total suspended solid and total hardness.
3. Using different ecological indices to assess the extent of contamination by some heavy metals Cd, Zn, and Mn in study area.
4. To determine the extent of increase studied metals concentrations in the river, the results of water and sediments were compared with Iraqi and international standards limit.

1.3 Literatures review

1.3.1 Heavy metals pollution world-wide problem

Among the inorganic contaminants of river water, heavy metals are getting importance for their non-degradable nature and often accumulate through tropic level causing a deleterious biological effect (Jain, 1978). There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or “Heavy metals”: Ag, An, As, Au, Bi, Cd, Ce, Cr, Co, Cu, Fe, Ga, Hg, Mn, Ni, Pb, Pt, Te, Tl, Sn, U, V and Zn (Glanze, 1996). According to Connell (1984) metals are defined as the metallic chemical element that has a relatively high density and are toxic or poisonous at a low concentration. Heavy metals are a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 or 5 times or more, greater than water (Hutton and Symon, 1986; Battarbee *et al.*, 1988; Nriagu, 1989; Garbarino *et al.*, 1995; Hawkes, 1997). Aycicek *et al*. (2008) mentioned that heavy metal toxicity is

one of the major current environment health problems and is potentially dangerous because of bio-accumulation through the food chain.

In general, the hazardous effects of these toxic elements depends upon the dietary concentration of element, absorption of the element by the body, homeostatic control of the body for the element and also the species of the animal involved (Underwood, 1977). The daily accumulation of heavy metals in our environment (particularly coastal waters) has intensified in recent years with population growth, industrialization and new technological developments (Ayenimo *et al*., 2005). Contaminants generally enter the rivers through two pathways: (a) identifiable point sources such as municipal and industrial waste water effluents and (b) diffuse source closely related to the meteorological factors. Major diffuse sources include surface runoff, erosion, and the atmospheric deposition. Both point and diffuse sources contribute to the total contaminant load of the rivers (Barcel'o, 2004).

Some heavy metals like (Fe, Zn, and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended. However, some others like (As, Cd, Pb, and methylated from of Hg) have been reported to have no know bio-an importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic (Holum, 1983; Fosmire, 1990; McCluggage, 1991; Ferner, 2001; EU, 2002; Nolan, 2003; Young, 2005). Even for those that have bio-importance, dietary intakes have to be maintained at regulatory limits, as excesses will result in poisoning or toxicity, which evident by certain reported medical symptoms that are clinically diagnosable (Fosmire, 1990; Nolan, 2003; Young, 2005). Various environmental factors like temperature, pH, water hardness, dissolved oxygen, light, salinity and organic matter can influence the toxicity of metals in solution (Bryan, 1976). CIS (1999) revealed that heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels, and damage to

blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Al-Zheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated log-term contact with some metals or their compounds may even cause cancer. Therefore the monitoring for these metals is important for safety assessment of environment and human health in particular (Kar *et al*., 2008). Heavy metals in aquatic environment can remain in solution or in suspension and precipitate on the bottom or be taken by organisms (Zare and Ebadi, 2005).

1.3.2 Heavy metals in water

Globally, there is an increasing awareness that water will be one of the most critical natural resources in future. The water is an essential requirement of human and industrial development and it's the most delicate part of the environment. Therefore, a continuous monitoring of water quality is very essential to determine state of pollution in our rivers.

Campbell and Tessier (1996) mentioned that heavy metals contamination is widespread in different Iraq aquatic systems. Water pollution by trace metals is an important factor in both geochemical cycling of metal and in environmental health. Trace amounts of heavy metals are always present in fresh waters from terrigenous sources such as weathering of rocks resulting into geo-chemical recycling of heavy metal elements in these ecosystems (Muwanga, 1997; Zvinowanda *et al.*, 2009). River running through urban areas has also been faced water quality issues due to discharge of untreated domestic sewage, municipal wastes and industrial effluents into then leading to increase the metallic toxicity in the river waters (Venugopal *et al*., 2009; Sekabira *et al*., 2010). Miller *et al*. (2003) revealed that heavy metals are persistent in surface waters in the form of colloidal, particulate and dissolved forms and rivers are known as the dominant pathway for the transport of

metals. Trace metals may become significant pollutants of many small riverine systems (Dassenakis *et al.,* 1998). Trace elements are easily influenced by environmental factor such as runoff, groundwater, dissolution from sediment, deposition from atmosphere and anthropogenic pollutants (Papafilippaki *et al.,* 2008). Metals in minerals and rocks are generally harmless and only become potentially toxic when they dissolve in water (Malhat, 2011).

1.3.3 Heavy metals in sediments

As important component of water environment, river sediment is not only the place where pollutants accumulate from the water body, but also it is a secondary pollution source which has a potential impact on water quality (Wang *et al.,* 2011). Sediment represents one of ultimate sinks for heavy metals discharged into aquatic environment. Therefore, sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Saeed and Shaker, 2008).

Ankley *et al*., (1992) were pointed that heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds. In aquatic ecosystems heavy metals are accumulated in sediments, where may reach concentrations several orders of magnitude greater than in the overlying water (Bryan and Langston, 1992). According to Aydinalp and Marinova (2003), heavy metals in soil may be found in one or more of the following forms:

a) Dissolved (in soil solution).
b) Exchangeable (in organic and inorganic components).
c) As structural components of the lattices of soil minerals.
d) As insoluble precipitates with other soil components.

The first two forms are available to the plants, while the other two are potentially available in the longer term. Groot *et al.* (1982) noted that under

natural condition, the concentrations of metals in sediments reflect the occurrence and abundance of a mixture of material in puts from different sources including eroded rocks and soils, swage and soil waste particles, atmospheric fallout and autochthons formation in the catchment area of the relevant rivers. The sediments play an important role as it has along residence time, therefore is an important source for the assessment of an anthropogenic contamination in rivers (Förstner and Wittman, 1983; Jain *et al*., 2005).

In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediment contamination. Due to the ecological importance and the persistence of pollutants in the aquatic ecosystem, sediments are more appropriate to be monitored in environmental evaluations and understand their potential toxic impacts (VonGunten *et al.*, 1997; Kwon and Lee, 2001; Ghrefat and Yusuf, 2006; Cesar *et al.*, 2006).

Förstner and Waittman (1983) noted that contaminants are not necessarily fixed permanently by the sediments, and under changing environmental condition they may be release to water column by various processes of remobilization. Sediment pollution, especially from heavy metals, has an important impact on water environment and a director potential threat on human and aquatic (Wang *et al.*, 2011).

Many researchers have used sediments to study the pathway of metals over time of sedimentation among them (Karbassi, 1989; Lee and Cundy, 2001; Weis *et al.*, 2001; Al-Masri *et al.*, 2002; Borretzen and Salbu, 2002; Bellucci *et al.*, 2003; Bertolotto *et al.*, 2003). Many researchers have conducted several studies of pollution of sediments with heavy metals in Tigris and Euphrates Rivers in Iraq such as Rabee *et al.* (2009). Other studies of Al-Lami and Al-Jaberi (2002); Al-Juboury (2009) were concerned with the heavy metals concentrations in the upper- mid region and Northern of Tigris River. While, Salih (1982) studied the geochemistry of Tigris River from Baghdad to Qurna, and other work of Kassim *et al.* (1997) in Euphrates River.

In other region Salati and Moore (2010) recorded the abundance of heavy metals decreases as Mn > Cr > Pb > Ni > Zn > Cu > Cd in sediment of Khashk River in Shiraz, southwest Iran. Lin *et al.* (2008) studied the sediments of second Songhua River in China and they showed that the concentrations of Co, Cr, and Ni in the sediment were generally only slightly higher than or equal to their background values, while the concentrations of Cu, Pb, and Zn were significantly higher than their background values.

1.3.4 Heavy metals in fishes

Fishes represent the peak of consumers in water system. Fishes have ability to collect these metals in concentrations higher than water and sediments due to feed on organic materials in aquatic environment (Olaifa *et al.*, 2004). Fishes have been found to be good indicators of the heavy metal contamination levels in aquatic systems because they occupy different atrophic levels (Burger *et al.,* 2002; Karadede-Akinand and Ünlü, 2007).

The amount of the toxic elements in fish is dependent on the concentration levels of these elements in the food and the habitats of fish, and the detoxification rate of metals (Urena *et al.,* 2007). According to Burger *et al.* (2002) there are two main routes of heavy metals exposure:

1. The primary route of intake of these chemicals in fish species is via gill or transport of dissolved contaminants in water across biological membranes and ionic exchange …etc.
2. The secondary route is through intestine by food or sediment particles with subsequent transport across the gut (Newarman, 1998).

The food may also be important source for heavy metal accumulation in fish (Javed and Hayat, 1996; Clearwater *et al.,* 2000). In aquatic ecosystem, metals are transferred to the fish through food chain that could ultimately affect the health of people consuming this fish.

Accumulation of these metals in the bodies of fish affected by different factors such as pH, water hardness and level of pollution in the surrounding

water added to the age and physiological situation of fish (Förstner and Wittman, 1981; Van den Broek *et al.,* 2002). Industrial and domestic waste containing heavy metals and hydrocarbon accumulate in aquatic food chains as possible to cause acute and chronic damages in fish communities and lead to reduce ability to growth and reproduce (Schulz and Martins, 2001).

Bioaccumulation and magnification are capable of leading toxic level of metals in fish even when the exposure is low. Structure of food chains in aquatic system is complex in compared to the dry land; where a small mass in aquatic environment is possible occurring significant changes, making it more sensitive to the impact of pollution (Förstner and Witman, 1981). According to Rapid bio-assessment protocols in USA: the advantages of using fish as bio-monitoring are:

1. Fishes are good indicators of long-term (several years) effects and broad habitat conditions because they are relatively long-lived and mobile (Karr *et al*., 1986).
2. Fishes assemblages generally include a range of species that represent a variety of trophic levels (omnivores, herbivores, insectivores, planktivores, piscivores). They tend to integrate effects of lower trophic levels; thus, fish assemblage structure is reflective of integrated environmental health.
3. The consuming of fishes by humans, were making them important for assessing contamination.
4. Fish are relatively easy to collect and identify to the species level. Most specimens can be sorted and identified in the field by experienced fisheries professionals, and subsequently released unharmed.
5. Environmental requirements of most fishes are comparatively well known. Life history information is extensive for many species, and information on fish distributions is commonly available.
6. Aquatic life uses (water quality standards) are typically characterized in terms of fisheries (cold water, cool water, warm water, sport, forage).

Monitoring fish provides direct evaluation of “fish ability” and “fish propagation”, which emphasizes the importance of fish to anglers and commercial fishermen.

7. Fish account for nearly half of the endangered vertebrate species and subspecies in the United States (Warren and Burr, 1994).

Fish is a source of cheap of food in various regions of world. Therefore, fish meat has a special nutritive value due to it is content of high quality proteins, fats rich in poly unsaturated fat acids with a high efficiency in the human body, vitamins (especially A and D) and a high level of mineral such as iron, phosphor, potassium, and magnesium (Banu, 2005).

1.3.5 Heavy metals in *Barbus xanthopterus*

The common name of *B. xanthopterus* fish is Ghattan fish that attributed to herbivorous Cyprinidae family; they are major component of Eurasian temperate fresh water fauna (Coad, 1998). The role of this family within fresh water ecosystems is therefore central and to date. The genus of *Barbus* constitutes is dominant component of Cyprinids family, with more than 800 species spread over Europe, Africa, Asia (Wang *et al.,* 2004).

B. xanthopterus spread in Tigris, Euphrates Rivers and all their tributaries, lakes and reservoirs. It reduces in number at local marshes and southern regions. Classification features represented at body is elongated and compressed, total length is 4.7 times of the head, mouth is sub-inferior, with two pairs of barbells which the inferior is slightly longer than the superior, lips are thick, eyes are small, scales are small, brownish on sides and belly is lighter (Al-Rudainy *et al.,* 2008). It is commercial fish with desirable taste, become wide spread in moderate-enrichment with oxygenated water, tolerate salinity reaches 8 g/l, the governmental sector works to propagate such species and release their fries to the water bodies to compensate for their diminishing number. It reach sexual maturity in 4 years with a length of 50 cm and a weight of 1500 g, spawn starts from April to late of May on gravel

beds and dig small nests in the gravel, deposit their eggs on the nest, water depth is 1/3-1 meter, absolute fecundity ranges from 100,000 to 260,000 egg per season (Al-Rudainy, 2008).

Several studies have shown that heavy metals accumulate in specific sites in the body rather than being distributed evenly throughout. Nussey *et al.* (2000) studied bioaccumulation of Cr, Mn, Ni, and Pb in the different tissues of a cyprinid fish, namely the moggel (Labeoumbratus) from Witbank Dam in the upper Olifants River catchment, and found bioaccumulation of Cr, Mn, Ni and Pb varied between the gills, liver, muscle and skin. The gills generally had the highest metal concentrations, due to their intimate contact with the environment and their importance as an effect of ionic and osmotic regulation. The liver, in its role as a storage and detoxification organ, can also accumulate high levels of metals. Muscles and skin accumulated much less metal concentrations. These two organs must be included in bio-monitoring programmes because they are consumed by the general public.

Salman *et al.* (2007) studied concentration of nine heavy metals in muscles of fish *Barbus luteus*; *Aspius vorax*; *Barbus grybus*; and *Hypophthalmicthyes molotrix* were collected from Euphrates River between Hindia dam and Al-Kufa city, and this study showed

a. Differences in concentration of heavy metals in the muscles of the fishes.
b. Some of these metals were appeared in high concentration (Cd, Cr, Mn, and Fe).
c. The Fe was accumulated in muscles of fish with the highest level followed by the levels of Zn, Mn and Cu.
d. *B. luteus and B. grybus* have more ability to accumulate heavy metals in their muscles, some of heavy metals apparent significant difference among study seasonal such as Cd, Cu, Fe, Mn, Ni, and Pb.

e. The study found significant correlation among some heavy metals like Fe, Co, and Cr, while an opposite correlation was found among other metals Cd, Cu, Ni, Mn this referred to variety in pollution source with heavy metal in the river and made fish as a good bio-indicator to study the pollution.

In Jordan, Al-Weher (2008) studied levels of heavy metal Cd, Cu and Zn in muscle, bone, skin, scales and gills of three fish species (*Oreochromis aureus*, *Cyprinus carpio* and *Clarias lazera*) collected from northern Jordan Valley, and he found *O. aureus* have the lowest levels of both Cd, and Cu metals in all tissues except gills. The other two fish species, *C. carpio* and *C. lazera*, showed less difference in their heavy metal levels. Cd and Cu recorded lowest levels in muscle and their highest levels in gills. *C. carpio* fish species showed high values of Cu metal in all organs, except muscles. *O. aureus* accumulated the highest level of Zn in all organs particularly in their skin (432.11±152.14 mg/ kg d. w.).

Uysal *et al.* (2009) studied the comparison of heavy metal accumulation ratios for muscle, sink, gill, liver and intestine tissues of some Cyprinidiae species (*Carassius carassius, Condrostoma nasus, Leuciscus cephalus,* and *Alburnus alburnus*) in Enne Dame lake in Turkey, and they found the accumulation level of the heavy metal copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), cobalt (Co), magnesium (Mg), nickel (Ni), chrome (Cr) and boron (B) in muscle were generally lower than other tissues, but there were some exceptions, Cd level in the muscle of *C. carassius* was higher than the permissible limit stated by Turkish legislation, FAO and WHO.

In southwest of Iran, Alhashemi *et al.* (2012) studied the trace elements (Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) in different tissues of three commonly available fish species in wetland ecosystem, and they found that mean concentrations of trace elements (except Ni and Co) were high in liver and gills of *Barbus grypus*. Also trace elements had the most accumulation in

liver of *Barbus sharpeyi* except for Cd (0.26 mg/kg dry wt.) and Mn (13.45 mg/kg dry wt.) that were high in gills. Beside, kidney is determined as target tissue for Ni and V in *B. grypus* and for Pb in *Cyprinus carpio*, due to their high concentration. Zn levels in all tissues of *C. carpio* showed the highest concentrations in comparison to other fish species.

Another study by Alhas *et al.* (2009) on determination heavy metal concentrations in muscle, liver, kidney and gill of *Barbus xanthopterus* and *Barbus rajanorummystaceus,* in the Atatürk Dam lake (Turkey), they noticed heavy metal concentrations vary significantly, depending on the type of the tissue in fish species. The metal accumulation in the liver, kidney and gill of *B. xanthopterus* and *B. rajanorummystaceus* was found to be quite high in comparison with that in the muscle. The distribution patterns of Fe and Co in tissues of *B. xanthopterus* follow the order: kidney >liver > gill > muscle; Zn and Cu follow the order: liver > kidney > gill > muscle; Mn and Ni follow the order: gill > liver > kidney > muscle; Cr follow gill > kidney > liver > muscle; Pb follows the order: liver > gill > kidney > muscle. In *B. rajanorummystaceus* tissues, Fe follows the sequence: liver > kidney > gill > muscle; Zn, Cu and Mn follow the sequence: gill > liver > kidney > muscle; Pb, Co and Ni follow the sequence: gill > kidney > liver > muscle.

In India, Vinodhini and Narayanan (2008) determinate the bioaccumulation of heavy metals in various organs of fresh water fish *Cyprinus carpio* were collected from ponds of southern districts of Tamilnadu and they found the order of heavy metal accumulation in the gills and liver was Cd > Pb > Ni > Cr and Pb > Cd > Ni > Cr. Similarly, in case of kidney and flesh tissues, the order was Pb > Cd > Cr > Ni and Pb > Cr > Cd > Ni. In all heavy metals, the bioaccumulation of lead and cadmium proportion was significantly increased in the tissues of *C. carpio* (common carp).

Olgunoğlu and Olgunoğlu (2011) studied seasonal variation of some trace metals (Pb, Cd, Hg, Cu, Zn and Fe) in the muscle tissues of two

commercially valuable freshwater fish species (*Silurus triostegus* and *Barbus grypus,* Heckel, 1843) from Atatürk Dam Lake (Turkey), and the obtained results showed the highest Cd and Zn levels were recorded in summer for the two fish species. The highest Pb and Hg levels were recorded in winter and autumn, respectively. Fe and Cu levels which are under detection limit in *S. triostegus*. However, Fe and Cu were at the highest level during summer and autumn mainly in *B. grypus.*



Figure (1): ***Barbus xanthopterus*** **(Heckel, 1843)**

1.3.6 Selected heavy metals for this study

1.3.6.1 Cadmium (Cd)

Cadmium is a few of elements spread in nature and can be considered as trace elements in view of the lack of focus in rocks, sediments, water and air, and notes an increase in concentration only in the case of a human activity or agricultural population or industrial (Al-Bassam, 2011). Cadmium is a common impurity as complex oxides, sulfides, and carbonates in zinc, lead and copper ores, and it is most often isolated during the production of zinc. Some zinc ores concentrates from sulfidic zinc ores contain up to 1.4 % of cadmium (Finkelman, 2005).

-The sources: The sources of cadmium in the aquatic environment are from natural weathering processes, mining, metal smelters, industries, agricultural use of sludges, fertilizers and pesticides, burning of fossil fuels, and the deterioration of galvanized materials and cadmium-plated containers (Anon, 1996). The average concentration of cadmium in the lithosphere is ~0.1 μg/g (Callender, 2003). Concentrations in pristine areas are < 0.2 μg/g with levels exceeding 100 μg/g at severely contaminated sites (Naidu and Morrison, 1994). Cadmium reaches into the blood stream by eating and drinking cadmium-contaminated food or water and by breathing cadmium contaminated air. It is employed in several industrial processes such as:

a. Protective coatings (electroplating) for metals like iron.
b. Preparation of Cd-Ni batteries, control rods and shields within nuclear reactors and television phosphors.

-The effects: The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones. Acute effects of inhalation are bronchitis and toxemia in the liver. Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small air sacs of the lungs become distended and eventually destroyed reducing lung capacity (Ansari *et*

al., 2004). There are several morpho-pathological changes in the kidneys due to long-term exposure to cadmium. Increasing intakes of zinc can reduce the renal toxicity of cadmium. An exposure to cadmium increases calcium excretion thus causes skeletal demineralization, probably leading to increases in bone fragility and risk of fractures (Wu *et al.*, 2001).

Cadmium and its compounds are currently classified by IARC as a Group 1 carcinogen for humans. Occupational human exposure has been correlated with lung cancer (IARC, 1993; IARC, 2010). Cadmium exposure, during human pregnancy, leads to reduced birth weights and premature birth (Henson and Chedrese, 2004).

1.3.6.2 Zinc (Zn)

Zinc is an essential micronutrient for all organisms as it forms part of the active site in various metalloenzymes. In most waters, the zinc (II) as oxidation state of zinc is toxic to aquatic organisms at relatively low concentrations. The greatest dissolved zinc concentration occurs in low pH, low alkalinity and high ionic strength solutions (Anon, 1996). Zinc is a very common environmental contaminant and it is commonly found in association with lead and cadmium (Denton *et al.*, 1997; Finkelman, 2005).

-The sources: The major sources of zinc in the aquatic environment are the discharge of domestic waste waters; coal-burning power plants; manufacturing processes involving metals; and atmospheric fallout (Denton *et al.*, 2001). Approximately one third of all atmospheric zinc emissions are from natural sources, the rest come from nonferrous metals, burning of fossil fuels and municipal wastes, and from fertilizer and cement production (Denton *et al.*, 2001; Callender, 2003).

The average zinc content of the lithosphere is approximately 80 μg/g; sediments from uncontaminated waters typically contain zinc concentration in the order of 5-50 μg /g (Callender, 2003).

-The effects: Taking large amount of zinc for several months may cause anemia, damage to pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol (Finkelman, 2005).

1.3.6.3 Manganese (Mn)

Manganese is a naturally occurring element in the environment. It comprises about 0.1% of the earth's crust (NAS, 1973). Food is usually the most important route of exposure for humans. Manganese is an essential micronutrient for plants and animals. It is a functional component of nitrate assimilation and an essential catalyst of numerous enzyme systems in animals, plants and bacteria. The concentration of dissolved manganese is influenced by changes in redox potential, dissolved oxygen, pH and organic matter (Anon, 1996). Manganese in surface water can be oxidized or adsorbed to sediment particles and settle to the bottom. Manganese in soil can migrate as a particulate matter to air or water, while the soluble manganese compounds can be leached from the soil. Manganese does not occur naturally as a base metal but is a component of more than 100 minerals, including various sulfides, oxides, carbonates, silicates, phosphates, and borates (NAS, 1973). Accumulation of manganese in soil usually occurs in the subsoil and not on the soil surface (WHO, 1981).

-The sources: It is found in rock, soil, water, and food. Thus, all humans are exposed to manganese, and it is a normal component of the human body. Manganese is released to air mainly as particulate matter, and the fate and transport of the particles depend on their size and density and on wind speed and direction.

Some manganese compounds are readily soluble in water, so significant exposures can also occur by ingestion of contaminated drinking water.

-The effects: Chronic inhalation exposure to manganese affects negatively on lungs, nervous system, and reproductive system, although affects on other organ systems (Erdogan, 2009).

1.3.7 Assessment of heavy metals pollution in sediments

The presence of metals in aquatic ecosystem in excess of natural background loads has become a problem of increasing concern. Heavy metals in environment may accumulate to toxic levels without visible signs (Olubunmi and Olorunsola, 2010).

In river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities (Shriadah, 1999; Singh *et al.,* 2002; Ali and Fishar, 2005). According to Caeiro *et al.* (2005) the concentration of metal contaminants can be classified into three types:

i. Contamination indices, which compare the contaminants with the clean or polluted stations measured.
ii. Background enrichments indices- which compare the results for the contaminants with the baseline or background levels.
iii. Ecological risk indices, which compare the results of contaminants with sediment quality guidelines (SQG).

Environmental quality indices are a powerful tool for development, evaluation and conveying raw environmental information to decision makers, managers, technician's or for the public (Praveena *et al.,* 2007). In recent decades, different sediment metal assessment indices applied to marine and fresh water environments have been developed. Speneer and Macleod (2002) mentioned that sediment quality values are a useful to screen the potential for contaminants within sediment to induce biological effects and compare sediment contaminant concentration with the corresponding quality guideline. The pollution indexes evaluate the degree to which the effect an aquatic organisms and are mangers responsible for the interpretation of sediment quality (Farkas *et al.,* 2007).

In recent years, many assessment methods of heavy metal pollution were used according to the samples characteristics, which include contamination

factor and degree of contamination, ecological risk index, enrichment factor, geo- accumulation and pollution load index (Gong *et al.*, 2008).

1.3.7.1 Geo-accumulation index (I-geo)

To understand the current environmental status and the metal contamination with respect to natural environmental, approaches should be applied. A common criterion to evaluate the heavy metal pollution in sediments is geo-accumulation index (I-geo), which was originally defined by Müller (1979) to determine metals contamination in sediments, by comparing current concentrations with pre-industrial levels.

Rabee *et al*. (2009) studied five metal concentrations in Tigris and Euphrates River and they used geo-accumulation index (I-geo) to study heavy metals (Ni, Cu, Pb, Mn, and Cd). This study indicates that the surface sediments in studied stations were unpolluted to slightly polluted by Pb and Cd except the Cd in south of Baghdad station (moderately polluted), and (I-geo) for Cu indicate the sediments were unpolluted to slightly polluted in Tigris stations, and unpolluted in the Euphrates stations. On Tigris River sediments at Baghdad city, the study of Rabee *et al.* (2011) found slightly polluted with Pb and Cd, while unpolluted with Mn, Cu, and Ni, when they used geo accumulation index to assess the pollution with some heavy metals.

Ghrefat and Yusuf (2006) studied assessment of Mn, Fe, Cu, Zn, and Cd by using I-geo index in bottom sediments of Wadi Al-Arab Dam in Jordan. They found the results of I-geo index of samples were unpolluted with Mn, Fe, and Cu. They also observed the moderately polluted with Zn, and strongly to extremely polluted with Cd, as well as some of the diverted pollution with Zn, and Cd are probably due to anthropogenic sources near the site of the dam. Habes *et al.* (2011) studied assessment of heavy metals by using (I-geo) in sediment of Kafrain Dam in Jordan, and they found the results of (I-geo) reveal that the study area was not polluted with Ni, Co, Cr, Cu, and Mn; and

moderately to strongly polluted with Pb; but strongly to extremely polluted with Cd and Zn.

Cevik *et al.* (2009) found the results of geo-accumulation index revealed that sediments of Seyhan Dam in Turkey were strongly polluted in stations 1, 2, 4, and 5, while were moderately polluted in station 3 with Cd.

Moore *et al.* (2009) studied assessment of heavy metal contamination in surface sediment of Maharlu saline lake which located in the south west Iran, and they found the results of sediment were unpolluted with As, Cr, Zn, Fe, and Mn (average I geo< 0), unpolluted to moderately polluted with Cu, and Ni(0 < average I geo < 1), moderately to strongly polluted with Co (2 < average I geo < 3), strongly polluted with Cd (3 < average I geo < 4), and strongly to extremely polluted with Pb (4 < average I geo < 5).

In Turkey, Özkan (2012) studied eight metal concentrations in surface sediments of inner Izmir Bay, and he found that the I-geo index values for Zn, Hg, Cr, and Cd have decreased two contamination classes from 1994 to 2008. Whereas, Pb was remained in the same class and Cu was decreased only one class. Generally Cu, Zn, Pb, Hg, and Cr contaminations were below effects range medium values.

Xie *et al*. (2012) mentioned that soil pollution in Shuangqiao River Basin (China) was assessed with geo-accumulation index and the results showed that the soil pollution of Cd, Cu, and Zn was lighter, Cr, As was not polluted and Hg was most serious element in studied area.

1.3.7.2 Pollution load index (PLI)

Pollution load index (PLI) represents the number of times by which the heavy metal concentrations in the sediment exceeds the background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample (Priju and Narayana, 2006).

Study of Rabee *et al*. (2011) on assessment of heavy metals in sediments of Tigris River in Baghdad city by used pollution load index, they noticed the results of heavy metals concentrations were very low, and ranged between (0.301-0.970). These indicating that the studied stations in Tigris River were unpolluted by total of studied heavy metals (Ni, Cu, Pb, Mn, and Cd).

Saha *et al.* (2001) studied pollution load index of (Cu, Zn, Fe, Mn, Pb, and Cd) in sediment of Jagannath canal in northern Sundarbans of West Bengol and found the mean PLI values of station 1, 2, and 3 were 1.63±0.10, 1.70± 0.09 and 1.79± 0.10, respectively, suggesting that station 3 was highly polluted with trace metals, which was due to its location nearest to the sewage out fall point calculate metropolis. Another study by Chakarvarty and Patgiri (2009) used pollution load index to assess heavy metals in sediments of Dirkong River in India and demonstrated lower values of PLI of implying no appreciable input from anthropogenic sources. Therefore, decrease in PLI values downstream indicating dilution and dispersion of metal content.

In the core sediment of a tropical wetland system in India, Harikumar *et al.* (2009) found that the PLI values and toxic unit showed a high pollution load at station Kuppapuram (18/v), while in the center of lake; the pollution of water was low to moderate range according to threshold effect level and probable effect level values.

1.3.7.3 Contamination factor (C_f) and degree of Contamination (C_d)

Saha *et al.* (2001) studied contamination factor (C_f) in sediment of Jagannath Canal in northern Sundarbans of West Bengol. This study indicated that the contamination with Cd in the soil, and the values considered very high in comparison to other studied metals. In Iran, Moore *et al.* (2009) studied ten metal concentrations in surface sediments of the Mahalu saline lake, and they found the metals can be divided into three different groups:

a. With regard to Co, Pb, and Cd, the Cf values of these metals were (11.1, 29, and 8, respectively); thus the Maharlu lake was highly polluted with these metals, and they were mainly from anthropogenic sources.
b. With respect to Cu, Zn, and Ni, the Cf values of these metals were (2, 1.1, and 2, respectively; thus the Maharlu lake was moderately polluted with these metals, and they were from both natural and anthropogenic sources.
c. Regarding to Cr, As, Fe, and Mn. These elements had Cf (0.32, 0.91, 0.63, and 1.5, respectively; thus the Maharlu lake was not polluted with these metals, and they were mainly from natural sources.

Another study by Harikumar *et al*. (2009) on assessment of heavy metals pollution by using C_f in sediments of a tropical wetland system, and they noticed that all stations except 15/v indicated moderate degree of contamination, the station 15/v had low degree of contamination. In Bangladesh, Saha and Hossain (2011) studied five metal concentrations in Buriganga River sediments and they used Cf to assess the pollution, and on the basis of mean values of Cf, sediments were enrichment for metals in the following order: Cu > Cd > Pb > Zn > Cr. On surface sediments of inner Izmir Bay at Turkey, Özkan (2012) studied eight metal concentrations and his results indicated that contamination of surface sediments was dominated by Pb, Hg, Cd, Zn and a lesser extent Mn, Cu, Cr and Fe.

1.3.7.4 Enrichment factor (EF)

The enrichment factor is the relative abundance of a chemical element in a soil compared to the bedrock. Enrichment factor is a convenient measure of geochemical trends and is used for comparison between areas (Hernandez *et al.,* 2003). In Tigris and Euphrates River, Rabee *et al*. (2009) mentioned that the calculated environment factor (EF) in all studied stations can be classified as minimal enrichment for Ni, moderate enrichment for Cu, and significant enrichment for the elements Pb and Cd. Study of Cevik *et al*. (2009) reported that enrichment factor of sediments of Seyhan dam in Turkey were treated as

a moderately severe enrichment with Cd and minor enrichment with Cr and Mn.

Lianfeng *et al.* (2010) recorded the highest EF of Cu, Pb, and Cr in sediments of Dalian, Northeastern in China and these results were 1.77, 2.16, and 1.89, respectively. Therefore, the sequence of contamination for Cu, Pb, and Cr in the analyzed samples was presented as the following Pb > Cr > Cu > and there was no obvious pollution of Zn in the studied area. Ghrefat and Yusuf (2006) studied assessment of Mn, Fe, Cu, Zn, and Cd by enrichment factor in bottom sediments of Wadi Al-Arab Dam in Jordan, and they showed that Mn and Cu were depleted by 0.76 and 1.33, respectively, whereas Cu, Zn, and Cd are enriched by 3.6 and 30, respectively.

In India, Chakravarty and Patgiri (2009) assess nine metals concentrations in Dikrong River by enrichment factor and found the mean concentration levels of Al, Fe, Ti, Mn, Zn, Cr, and Ni in sediments of all locations were lower than the background values, excepts concentration of Cu and Pb were uniformly higher than the background value. In study on Agbabu bitumen deposit area in Nigeria, Olubunmi and Olorunsola (2010) found the enrichment values of ten heavy metals (Fe, Cu, Mn, Cr, Zn, Hg, Pb, Cd, NI, and V) were higher in the dry season than in the wet season, and the values of EF ranged between 0.51 to 2.19 in sediment and this confirmed that the slightly heavy metal pollution of Agbabu bitumen deposit area, as well as the pollution in the study area was not due to anthropogenic activities.

Özkan (2012) studied assessment of Fe, Cu, Hg, Cd, Zn, Pb, and Cr by enrichment factor in sediments of inner Izmir Bay and found the values of Fe, Mn, Cu, Hg, and Cd were especially less than 5 (moderate enrichment and minor enrichment), while Zn, Pb, and Cr were very heavily enriched in studied area.

1.3.7.5 Potential ecological risk index

The potential ecological risk index is employed to calculate potential ecological risk factors of heavy metals so as to assess their pollution status in each layer of the sediments in the sections (Wang *et al.,* 2011). Liu *et al.* (2009) studied ecological risk of heavy metals in sediment of the Luan River source water and they observed when compared the results with soil background values of China, that both of Hg and Cd showed very strong potential ecological risk depending on the results of the study. In China, Lin *et al.* (2008) studied assessment of heavy metals by ecological risk index in sediment of the second Songhua River in China, and they found the surface sediment in the studied river section was classified as natural sediment without ecological risk for both of Cu, Cr, Ni, Pb, and Zn.

Sediment of Huai River in China (Jiangsu section) was classified as low potential ecological risk with Cd, As, Hg, Pb, Cu, and Zn (Huang *et al.*, 2004). Sediment in Hiahe River was characterized by low to moderate potential ecological risk with Cu, Cd, Pb, Zn, and Cr (Wang and Sun, 2005).

In north China, Wang *et al* .(2011) studied heavy metal concentrations in Drainage River sediments by using potential ecological risk and they found E^i_f for each studied heavy metal, the study results indicated that the contamination of Cu and Cd reach considerable and very high degrees of potential ecological risk, while the others had low potential ecological risk. Krupadam *et al.* (2006) studied assessment of heavy metals (Zn, Cu, Co, and Ni) by ecological risk index in sediments of Tapi estuary, and they found Zn produced the highest individual ecological risk among the studied metals due to this finding, the critical element would be concerning ecological hazard in the Tapi estuary.

1.3.8 Assessment heavy metals pollution in fish

1.3.8.1 Bioaccumulation factor (BAF)

In aquatic ecological risk assessment, bioaccumulation factor (BAFs) is used to quantify chemical accumulation in tissue relative to concentration in water or sediment (Thomann *et al.,* 1995; Fairbrother *et al.,* 2007). Bioaccumulation of metal in the tissue of interest or the whole organism the results from all environmental exposure media, including air, water, soil phases, and diet (Fairbrother *et al.,* 2007).

Alhashemi *et al.* (2012) studied determination of bioaccumulation factors (BAFs) by different tissue of fish species (*Barbus grypus*, *Barbus sharpeyi*, and *Cyprinus carpio*) with respect to elemental concentrations in sediment. BAFs results indicated that Zn, Pb, and Cu had higher BAF than other elements. In Kuwait Bay, Bu-Olayan and Thomas (2008) instigated to conduct toxicity and bioaccumulation tests of trace metals (Zn, Cu, Cd, and Fe) and they found bioaccumulation factors (BAFs) was sequence of Cd > Fe > Cu > Zn. for fish exposed for 60 day, and bioaccumulation exhibited increasing metal levels in liver followed by muscle tissue and gills.

In Tumkur (India) Nayaka *et al.* (2009) mentioned that bioaccumulation factor (BAF) for different heavy metals from water to fish was Cu (55000), Cd (2383), Fe (1887), Cr (909), Zn (881), Pb (320) and Ni (7320). In Enne Dame lake in Turkey, Uysal *et al*. (2009) mentioned that the bioaccumulation factors (BAFs) of Mn, Zn, Fe and Cu were remarkably high, and the BAFs of Mg, Cr, Co, and B were also fairly low or none.

Chapter two

Materials and methods

2.1 Description of the study area

The study area (Tigris River within Baghdad city) is located in the mesopotamia alluvial plain between latitudes 33°14'-33°25' N and longitudes 44°31'-44°17' E.

Tigris River is one of the most important twin rivers in Iraq, sharing with Euphrates River as the main sources for human use, especially for drinking water since they cross the major cities in the country. Tigris River is 1.850 km long, rising in the Taurus Mountainous of eastern Turkey about 25 km southeast of the city of Elazig and about 30 km from the headwaters of the Euphrates. The river then flows for 400 km through Turkish territory before becoming the border between Syria and Turkey. This stretch of 44 km is the only part of the river that is located in Syria. The remaining 1.418 km is entirely within Iraq (Isaev and Mikhailova, 2009). It has five tributaries inside Iraq; they are from north to south includes: Al-Khabour, Great and Lesser Zap, Al-Adaim and Diyala. All these tributaries, with the initial force provided by steep slopes, carry their erosion products into the plain, where they join Euphrates (Rzóska, 1980).

Tigris River is heavily dammed in Iraq and Turkey, to provide water for irrigating the arid and semi desert region bordering the river valley. Damming has also been important for averting floods in Iraq. Recent Turkish damming of the river has been the subject of some controversy, both for its environmental effects within Turkey and its potential to reduce the flow of water downstream. In addition, the study area is characterized by arid or semiarid climate with dry hot summers and cold winters; the mean annual rainfall is about 151.8 mm (Al-Adili, 1998). Tigris River enters Baghdad city at a distance of 5 km north of Al-Muthana Bridge, either a point of exit, about

3 km south of estuary of Diyala River, and a length between those two points about 58 km, the river divides Baghdad city into a right side (Karkh) and left (Rusafa) sections with a flow direction from north to south (Al-Adili, 1998). It has numerous river twists due to decrease in speed and precipitation (Toma, 1983). It is characterized by the presence of permanent large islands, such as the island of Abu Rameel, Al-Greaat and Al-Kadhmeya. The river includes a number of small seasonal islands, that arise as a result sedimentation of river, seasonal islands showing when water level of Tigris River is a low and sometimes in drought season and these islands covered with reeds and wild grasses, islands sink in the flood season and when the river levels will rise (Al-Shareefy, 2007).

The width and depth of Tigris River depend on the seasonal discharge of water and morphology of bed, during the low discharge seasonal (summer), the river is shallow 2-5 m deep and about 230 m wide, and the bottom nature ranged from rocks, stones and cobbles at the upper reaches to sand and clay at mid and lower reaches (Rzóska, 1980). Sewage industrial wastes of big cities, such as Baghdad and Mosul create a further load on Tigris River (Kassim *et al.,* 1997). In present study four stations were chosen from Tigris River in Baghdad city (Fig. 2-a), the longitudes and latitudes of studied stations were mentioned in Table 1.

Table (1): Latitudes and longitudes of study stations in Tigris River within Baghdad city

Stations	Latitudes (North)	Longitudes (East)
Al-Greaat S.1	33°23'4.734"N	44°19'59.683"E
Al-Atafia S.2	33°21'41.809"N	44°22'18.84"E
Bab Al-Mudhum S.3	33°20'48.659"N	44°22'11.785"E
Al-Rashid power plant S.4	33°16'59.347"N	44°27'18.692"E

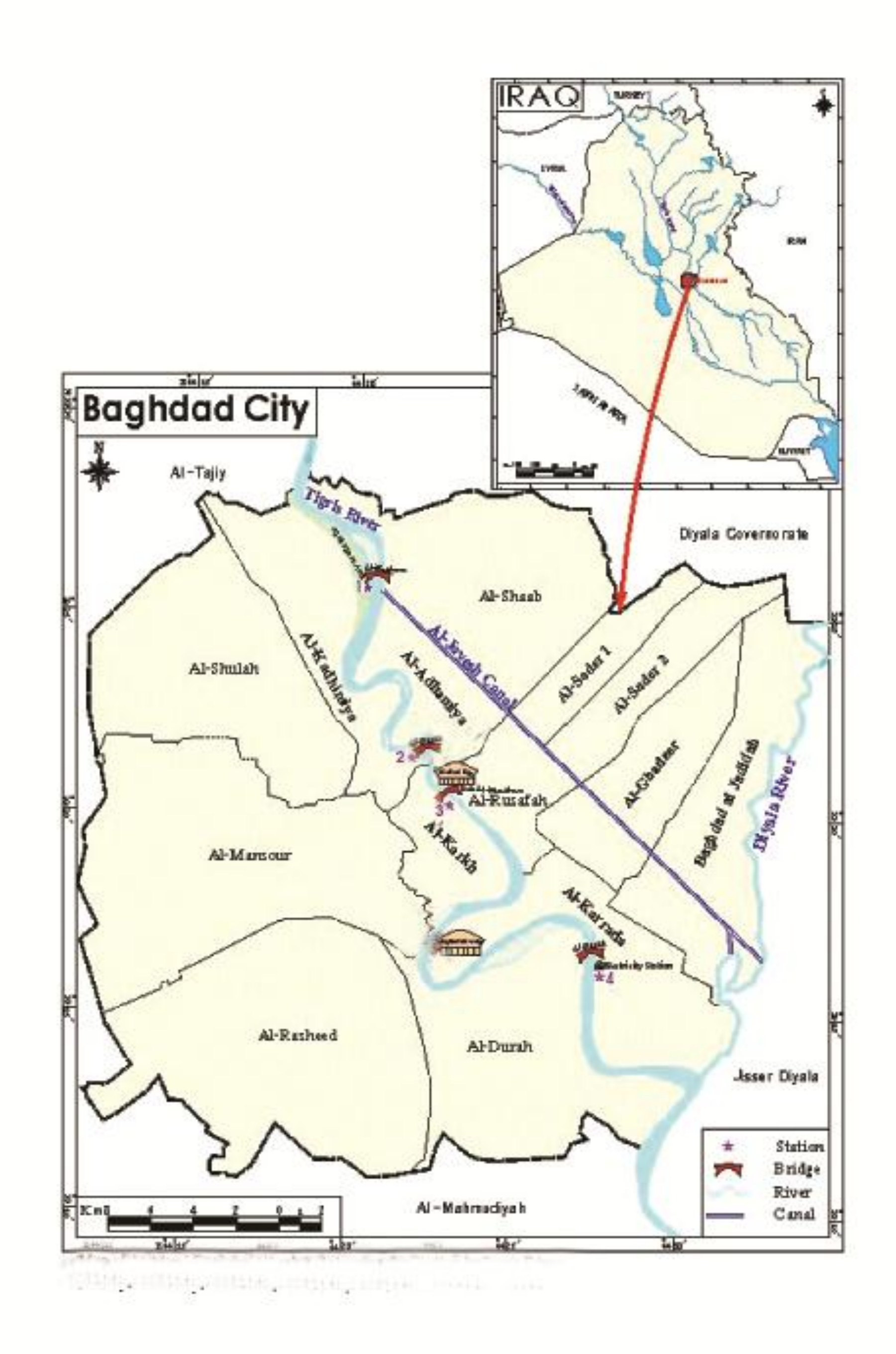


Figure (2-a): Tigris River along Baghdad city with the sampling stations. Source: Ministry of Water Resources, 2007. Map Scale 1/100000

1. Al-Greaat area: This station located under floating Bridge for pedestrians, nature of the area is agricultural and rich with palms groves on the edges. The depth of water at a distance of 1 m from the riverbank is 40 cm, and people visit this place to relax and presence restaurants. Therefore, we found food scraps and paper napkins near the river. Sediments of this station consist of clay, silt and sand (29.91, 22.73, and 47.36)% respectively. Sediments texture is sandy clay loam (Fig. 2-b).

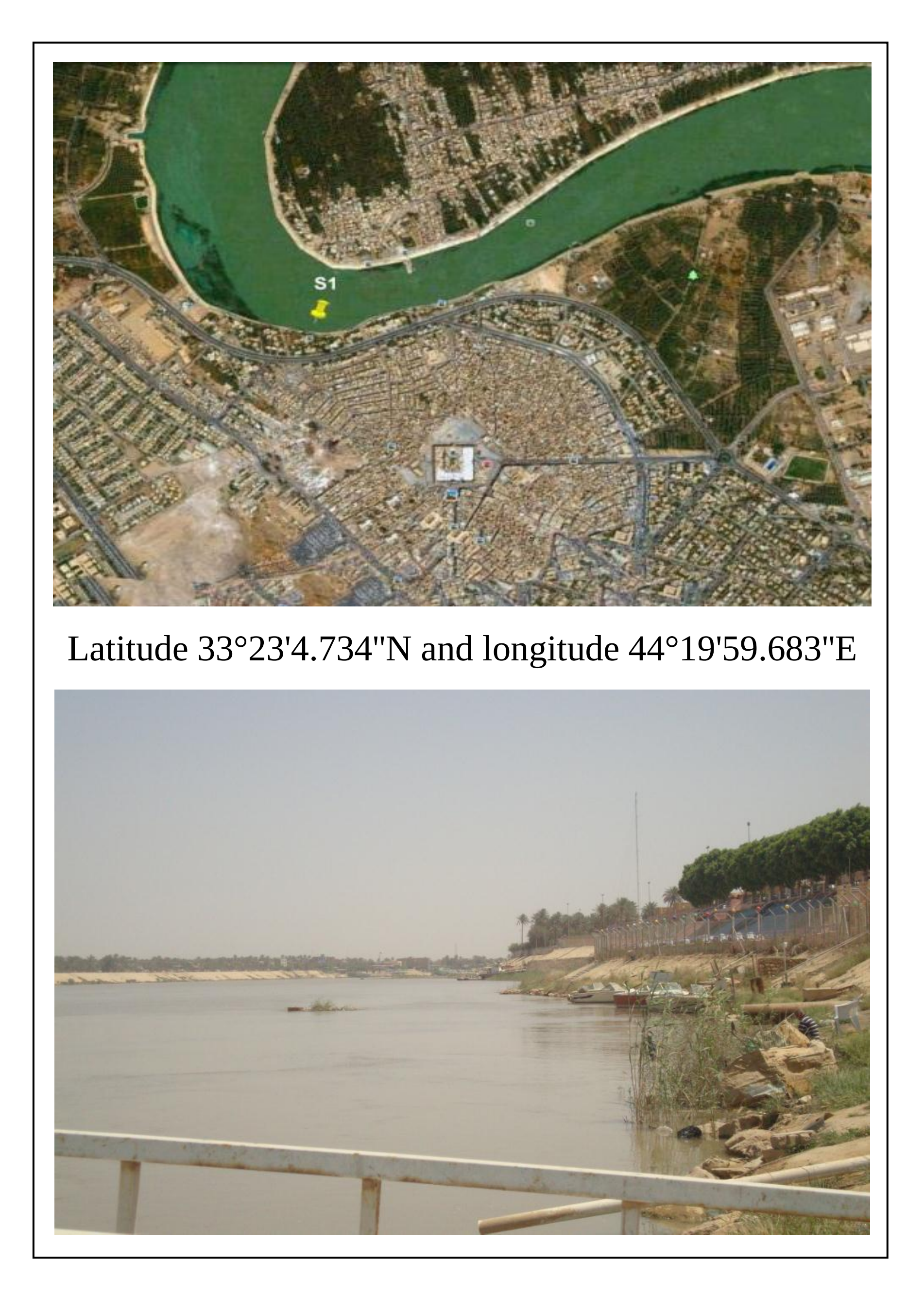
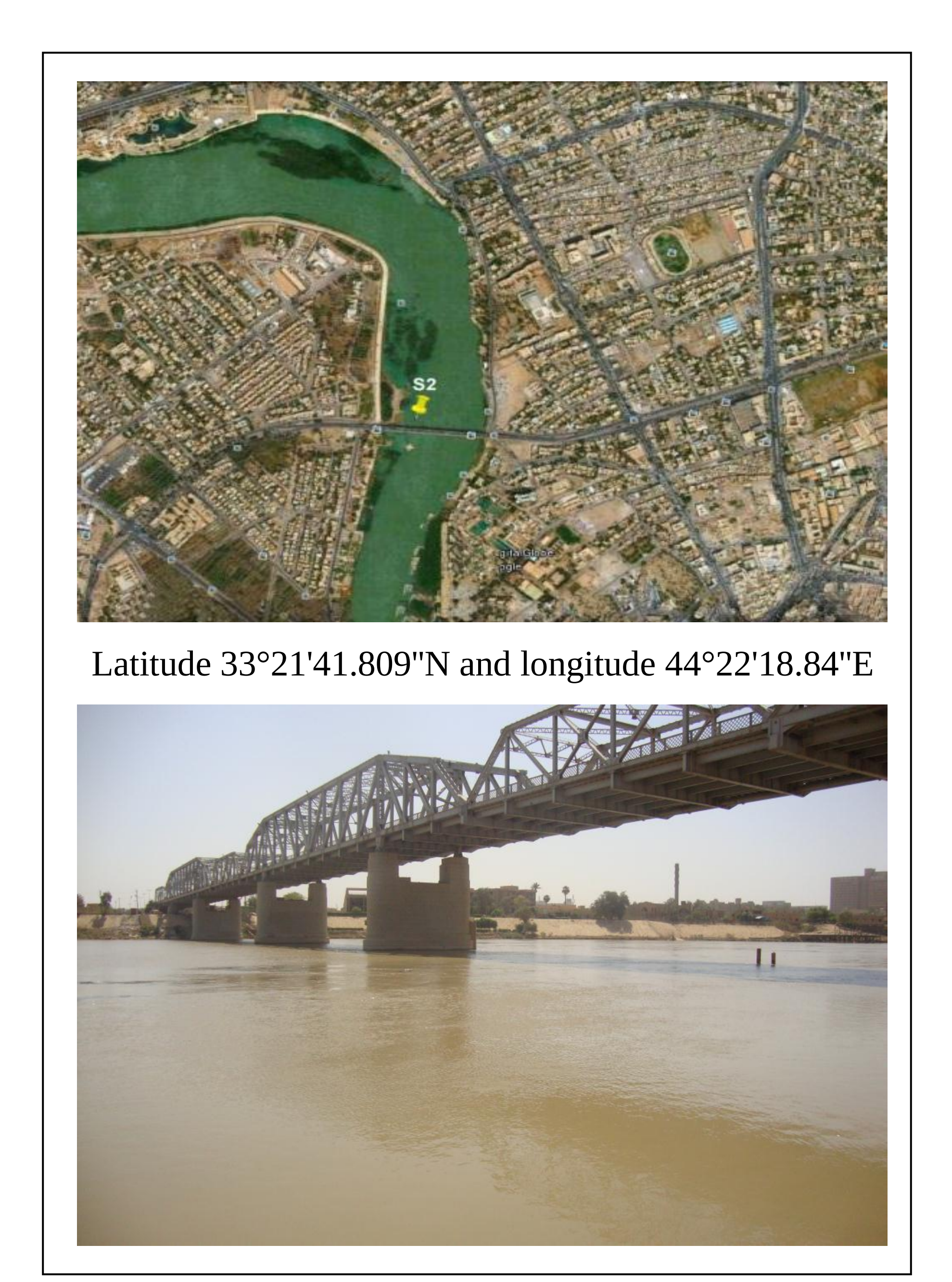


Figure (2-b) Station 1

2. Al-Atafia area: This station located under Al-Sarafia Bridge. In this station we do not found trees or a plant. The depth of water at a distance of 1 m from the riverbank is 35 cm. Sediments of this station consist of clay, silt and sand (26.53, 21.19, and 52.28)% respectively. Sediments texture is sandy clay loam (Fig. 2-c).



Latitude 33°21'41.809"N and longitude 44°22'18.84"E

Figure (2-c) Station 2

3. Bab Al-Mudhum area: In this region, Tigris River influence by residues of medical city which is located on the side of Al-Rusafa and activities of residential on the sides as well as the movement of fishermen and river navigation. The depth of water at a distance of 1 m from the riverbank is 50 cm. Sediments of this station consist of clay, silt and sand (30.25, 25.41, and 44.34)% respectively. Sediments texture is clay loam (Fig. 2-d).

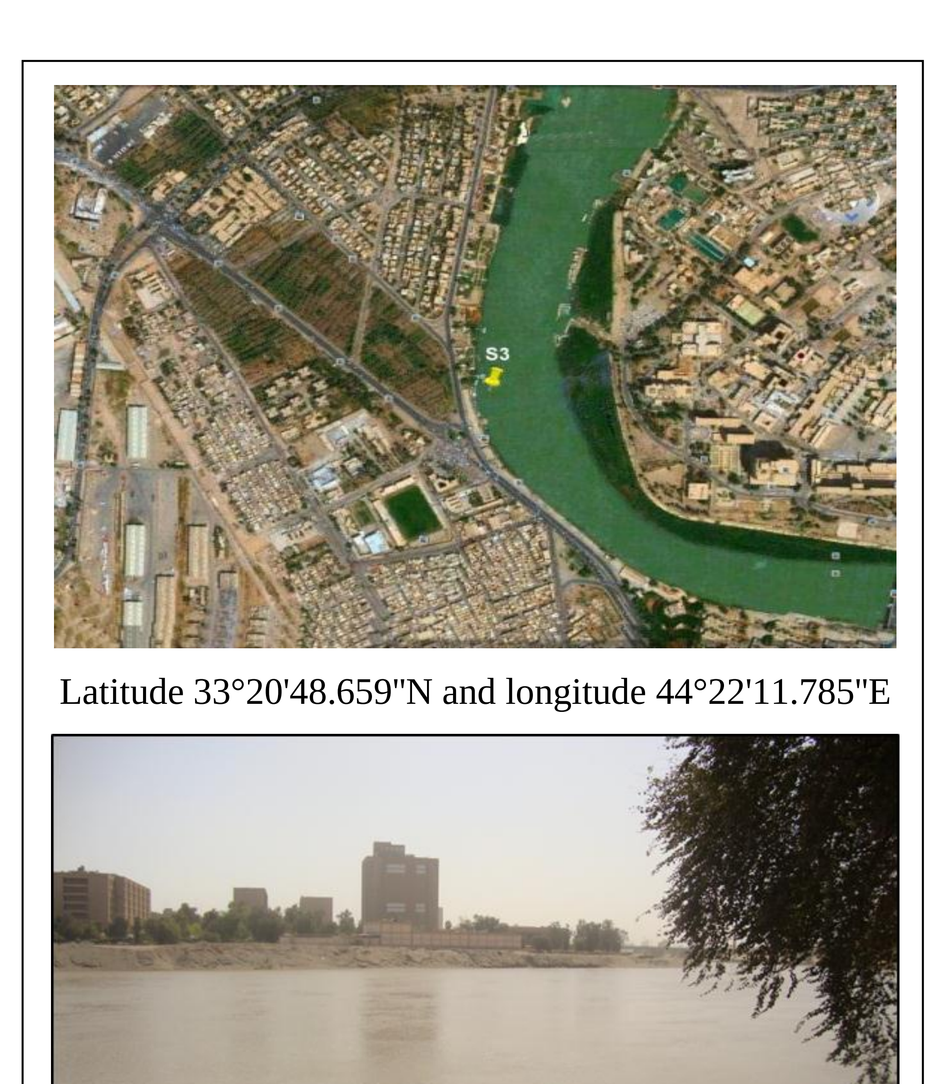


Figure (2-d) Station 3

4. Al-Rashid power plant: this station located before Al-Rashid water treatment plant and Rashid electrical plant .In this station large trees and wild plants on the riverbank were observed such as grasses and reeds. This station located in industrial area due to found many of factories on the edges of river such as oils factory. Water of Tigris River is used in production processes are also used as a way out for liquid wastes from factories. The depth of the water at a distance of 1 m from the riverbank is 50 cm. Sediments consist of clay, silt and sand (22.12, 19.34, and 58.54)% respectively. Sediments texture is sandy clay loam (Fig. 2-e).



Latitude 33°16'59.347"N and longitude 44°27'18.692"E



Figure (2-e) Station 4

2.2 Instruments and chemical materials for this study

There are many instruments and chemical materials were used, in order to test concentrations of studied heavy metals (Cd, Zn, and Mn) in water, sediments and fish, and Also, some physical and chemical characteristics (Table 2 and 3).

Table (2): A list of instruments that were used in field and laboratory work

Instruments	Model and Manufacturer
Millipore filter paper (0.45µm)	Whatman (England)
Thermometer	Zeal (England)
Distillation system	GFL 2001/4 (Germany)
pH/ EC/ TDS meter	SM801. SM802 (Germany)
Oven	Memmert (Germany)
Sensitive balance	Sartorius (Germany)
Filtration apparatus	Wattman (U K)
Flame atomic absorption spectrophotometer	PERKIN-ELMER 5000 (USA)
Flameless atomic absorption spectrophotometer	Shimadzu- GFA- 413 Graphite Furnace Atomizer (GFAAS) (Japan)
Muffle furnace	Bu Bu (USA) Que, LOWN, (USA)

Table (3): A list of chemical materials that were used in laboratory work

Materials	Model and Manufacturer
Nitric acid	Merck (Germany)
Hydrochloric acid	BDH (England)
De-ionized water	Local
H_2SO_4	BDH (England)
NaOH	BDH (England)
Na- thiosulfate	Anala R (England)
Erichrom black T (EBT)	Merck (Germany)
Ethylene Diamine Teteraacetic Acid EDTA-Na_2	Fluka (England)
$MgSO_4.7\ H_2O$	Merck (Germany)
NaN_3	BDH (England)
Potassium iodide	Merck (Germany)
Potassium dichromate ($K_2Cr_2o_7$)	Merck (Germany)
NaI	BDH (England)
Starch	Anala R (England)
Ammonium ferrous sulfate	Anala R (England)
NH_4Cl	AnalaR (England)
NH_4OH	Merek (Germany)

2.3 Field study

Air and water temperature were measured by using mercury thermometer 0-100^{0}C. The air temperature was measured in shade; while the water temperature was measured by immersed the thermometer under water surface about 15-20 cm for 3-5 minutes. The results expressed as Celsius degrees. Hydrogen Ion Concentration (pH), Electrical Conductivity (EC) and Total Dissolved Solid (TDS) were determined in field by using a portable pH/ EC/ TDS meter.

The results expressed as microsemins/cm (µs/cm) for EC and mg/l for measured TDS.

2.3.1 Sampling scheduling

Samples of water, sediments and fish species, *B. xanthopterus* were collected every two months for one year (from October, 2011up to August, 2012). Four stations were chosen on Tigris River in Baghdad city for this purpose. Station 1 (Al-Greaat), station 2 (Al- Atafia), station 3 (Bab Al-Mudhum) and station 4 (Al-Rashid power plant).

2.3.1.1 Water sampling

Surface water samples were taken from each station on Tigris River by using polyethylene containers (5 litters) under water surface about 20-30 cm after punning the container with river water, then kept at 15^{0}C in refrigerator.

2.3.1.2 Sediments sampling

Surface sediments samples of 10 cm thickness were taken in each station, using tool for digging, and quickly packed in polyethylene bags. The samples were kept in ice before being transported to the laboratory.

2.3.1.3 Fish sampling

Fresh water fish, *B. xanthopterus* were collected from (1, 3, and 4) stations which represent north, middle and south parts of river in Baghdad city. The samples were purchased from local fishermen at the spot. The fish

were killed by blow on head, then packed in ice and brought to laboratory on the same day. In order to minimize the difference in metal accumulation caused by the age of individuals, the body weights were between 900 to1500 gm and length were between30 to 40 cm. The present study was depending on Animal and Fish Research Center to confidence on the classification of fish.

2.3.1.4 Water samples for dissolved oxygen sampling

Water samples collected in sterile Winkler bottles 250 ml below the surface of water. 2 ml of manganese sulfate solution followed by 2 ml of alkaline iodide sodium azid solution were added to water samples to fix oxygen. Bottles were carefully closed with stopper to exclude air bubbles and mixed thoroughly by shaking the bottle. The formed precipitate was immediately taken to laboratory for analysis.

2.4 Laboratory studies

2.4.1 Heavy metals analyses

Heavy metals extraction from the filtered water of river, sediments and fish of *B. xanthopterus* was done by following procedures:

2.4.1.1 Extraction of heavy metals from filtered water

One liter of water sample was filtered by using Millipore filter papers (0.45 µm). These filter papers were washed with hydrochloric acid (5%), followed by de-ionized water and dried at 60^0C for 24hr; the filtered water was transferred to a beaker then acidified with 5 ml of concentrated nitric acid. The beaker was covered with a ribbed watch glass; the solution was heated on a hot plate (without boil) at 85^0C until the volume reduced to approximately 20 ml. The sample allowed to cool and transferred to 50 mL volumetric flask. The volume was completed with de-ionized water and let settle overnight to remove insoluble materials. The solution was kept in clean

polyethylene flasks. Finally, the solution was ready for reading by flame atomic absorption spectrophotometer (APHA, 1998).

Measuring final concentration:

$$E_{con} = \frac{A \times B}{C}$$

E_{con}: Concentration of metal in water (mg/l).

A: Concentration of metal in calibration curve (mg/l).

B: Final volume of sample (ml).

C: Initial volume of sample (ml).

2.4.1.2 Extraction of heavy metals from sediments

To measure the heavy metals (Cd, Zn and Mn) in sediments. In the beginning, the sediments were dried into Petri dishes in oven at (70-80)^{0}C for 1-2 day. The dried sediments were powdered by using agate mortar and pestle, and then the powder of samples was allowed to pass through 63 µm aperture size to remove larger particles. 1gm of sieved sediment was transferred to a beaker then digested with 10 ml of pure and concentrated HNO_3. The beaker was covered with watch glass and leaved overnight in hood and then heated on hot plate without boil with slightly mix until sample reached to near dryness. De-ionized water was added, and then filtered through filter paper with diameter 15.0 cm. The filtered solution completed to 50 ml by using de-ionized water and finally kept in polyethylene containers and stored in a refrigerator until analysis with flame atomic absorption spectrophotometer (APHA, 1998). Measuring final concentration:

$$E_{con} = \frac{A \times B}{D}$$

E_{con}: Concentration of metal in sample (µg/g).

A: Concentration of metal in calibration curve (mg/l).

B: Final volume of sample (ml).

D: Dry weight of sample (g).

2.4.1.3 Extraction of heavy metals from fish

Fish specimens of each station dissected for gills, intestine and muscles. About 50 gm of native organs were taken into crucibles and dried for 2 hr. at 70^0C in oven. Then burned by Muffle furnace at 450-500^0C for 4 hr. 1 gm of samples ash was putted into the beaker. 6 ml of concentrated HNO_3 and 2 ml of concentrated HCL were added into beaker, and then warmed into water bath at 70^0C for one hour with stirring to accelerate reaction to ensure complete digestion. The productive mass was cooled in room temperature and filtered by using filter paper (0.45 µm). The filtered solution completed to 25 ml with de-ionized water and finally kept in polyethylene container for analysis by flameless atomic absorption spectrophotometer (Tsoumbaris, 1990; Seady, 2001). Measuring finale concentration:

$$E_{con} = \frac{A \times B}{D}$$

E_{con}: concentration of metal in sample (µg/g).

A: concentration of metal in calibration curve (mg/l).

B: final volume of sample (ml).

D: dry weight of sample (g).

2.4.2 Physical and chemical measurements

2.4.2.1 Dissolved Oxygen (DO)

Winkler method was used to measure the dissolved oxygen. This method described by Boyd (1981), which summarized by fixing oxygen in field, and then added 2 ml of H_2SO_4 and bottle was shake thoroughly to dissolve the precipitate. Then was titrated against (0.0125 N) $Na_2S_2O_3.5H_2O$ (sodium thiosulphate solution) using 2 drops of starch solution as an indicator.

2.4.2.2 Total Suspended Solid (TSS)

The standard method that mentioned in APHA (1998) was used to determine the suspended particulate matter by washing filter paper (0.45μm) and then was dried at 105^{0}C for one hour, cooled and weight. 100 ml of sample was filtered and returned again to the oven, cooled, and then weight. TSS was calculated by using the following equation:

$$\textbf{TSS (mg/l)} = \frac{(A-B)\times 1000}{ml\ of\ sample}$$

A= weight of filter paper with residue mg.

B= weight of filter paper.

2.4.2.3 Total Hardness (TH)

Total hardness generally comes from $Ca^{+2}$and Mg^{+2}ions (Fairbridge, 1972). Total hardness measured by amount of calcium carbonate according to Boyd (1981). 100 ml of water sample was mixed with 2 ml of buffer solution (ammonia 25%) to make pH=10 and then 8 drops of indictor (Erichrom black T) were added to the mixture turned the color to wine red. The mixture was titrated with EDTA (0.01) N solution until the mixture color changed from wine red to pure blue. The total hardness was calculated according to following equation:

$$\textbf{Total Hardness as } CaCO_3 \textbf{ (mg/l)} = \frac{A\times B}{ml\ of\ sample}\times 1000$$

A: ml of EDTA used in titration

B: mg of $CaCO_3$ equivalent to 1ml of EDTA

2.4.3 Sediment analyses

2.4.3.1 Total Organic Carbon (TOC) in Sediments

The methods described previously by Hayward (1953) and ICARDA (1996). The method depended on oxidation of organic matter by potassium dichromate and the procedure is:

Briefly, 1 gm of sample was added to 10 ml of potassium dichromate solution and 20 ml sulfuric acid in 500 ml beaker. The mixture was allowed to stand for 30 minutes. Then 200 ml de-ionized water and 10 ml phosphoric acid, with 10-15 drops diphenylamine indicator were added to mixture. The final solution was titrated against ammonium ferrous sulfate to change color of mixture to metallic green color (end point). Blank was composed of all the materials used except the sample. The result was calculated as the following equation:

$$\mathbf{X = T - Blank}$$

$$\mathbf{F = \frac{10ml\ (K_2\,Cr_2\,O_7)}{Blank}}$$

$$\textbf{Percentage of oxidized organic carbon } (\%\ O_x\ .O.C.) = \frac{(X \times F)\ 0.28896}{\text{Sample used (g)}}$$

Percentage of Total Organic Carbon= 1.334× (% O_x .O.C.)
(%T.O.C.) mg/l

2.4.3.2 Soil Texture

It was determined by hydrometer analysis procedure that described previously by Hayward (1953); Lambe and Robert (1969).

1-Clay (%)

50 gm of sample was put in 500 ml beaker, then 75 ml Galgon (1N) [sodium hexametaphosphate $(Na2PO^{-}_3)_6$] was added. Then 125 ml P_2O_5 (0.4N) was added to mixture. The mixture was allowed to stand for 24 hour then mixed by magnetic stirrer for 10 minutes; the final solution was poured in to a cylinder of 1000 ml. The volume was completed to 1000 ml with distilled water and mixed by glass rod. Finally hydrometer system was used. The result was calculated by following equation:

$$V = \frac{\gamma s - \gamma w}{18U} \times D^2$$

As:

V= Speed of fall particles.

ɤs=Soil density.

ɤw= Water density.

D^2=Radius squired.

U = Viscosity factor.

2-Sand (%)

50 gm of samples were allowed to pass through metal sieve 0.5 mm aperture size. Sand obtained from sieve was dried by oven. The result was calculated according to the equation below:

$$Sand\ (\%) = \frac{sand\ (g)}{50} \times 100$$

3-Silt (%)

Silt was calculated by the equation below:

$$Silt\ (\%) = 100 - (Sand\ \% + Clay\ \%)$$

Finally, each of clay, sand and silt values (%) was applied as agricultural texture rectangle to classified soil texture.

2.5 Ecological indexes

2.5.1 Sediments pollution indexes

2.5.1.1 Geo-accumulation Index (I-geo)

Geo-accumulation index was determined by the following equation according to Müller (1969) which was described by Boszke *et al*. (2004).

I-geo = Ln (C_n / 1.5 B_n)

C_n = Measured concentration of heavy metal in the sediments of Tigris River.

B_n= Geochemical background value in average shale of element n (nature value of element n in crust of earth). The factor 1.5 is used for the possible variations of the background data due to lithological variations. I-geo was classified into seven grades listed below (Müller, 1969)

I-geo	I- geo class	Pollution intensity
≤ 0	0	unpolluted
0< I-geo ≤1	1	slightly polluted
1< I-geo ≤2	2	moderately polluted
2< I-geo ≤3	3	moderately severely polluted
3< I-geo ≤4	4	severely polluted
4< I-geo ≤5	5	severely extremely
> 5	6	extremely polluted

2.5.1.2 The Pollution Load Index (PLI)

The pollution load index (PLI) is obtained as concentration factors (CF). The CF obtained by dividing the concentration of each metal. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. The PLI obtained from each place. Generally pollution load index (PLI) as developed by Tomlinson *et al.* (1980) which is as follows:

CF = C metal / C background value

$$\mathbf{PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots \times CFn)}}$$

CF = contamination factor, n = number of metals.

C metal = metal concentration in polluted sediments.

C Background value = background value of that metal.

The PLI value > 1 is polluted, whereas < 1 indicates no pollution (Harikumar *et al.*, 2009). The world average concentration of Zn (95 µg/g), Mn (900 µg/g) and Cd (0.3 µg/g) reported for shale were considered as the background value (Turekian and Wedepohl, 1961).

2.5.1.3 Contamination Factor and Degree of Contamination

The contamination factor C_f and the degree of contamination were used to determine the contamination status of the sediment in the present study. C_f values are suggested for describing the contamination factor (Hakanson, 1980). Contamination factor calculated by following equation:

CF = C metal / C background value

CF = contamination factor.

C metal = metal concentration in polluted sediments.

C Background value = background value of that metal.

$C_f < 1$: low contamination factor; $1 \leq C_f < 3$: moderate contamination factor; $3 = C_f < 6$: considerable contamination factor; $C_f = 6$: very high contamination factor.

The degree of contamination (C_d) was defined as the sum of all contamination factors. The following terminology was adopted to describe the degree of contamination (C_d values) for the selected metals. $C_d < 6$: low degree of contamination; $6 = C_d < 12$: moderate degree of contamination; 12=

C_d< 24: considerable degree of contamination; C_d= 24: very high degree of contamination indicating serious anthropogenic pollution.

2.5.1.4 Enrichment Factor (EF)

The Enrichment Factors (EF) was calculated to evaluate the abundance of metals in sediments. Enrichment Factor (EF) calculated by the comparison of each tested metal concentration with that of a reference metals. Enrichment factors (EF) for mean metal concentration in sediments at all the stations was calculated and used for comparison by using the following equation:

$$EF = \frac{Cn\ (sample) / Cref\ (sample)}{Bn\ (background) / Bref\ (background)}$$

Cn (sample) = the metals concentration (µg/g) in a sample.

Cref (sample) =the reference metals concentration (µg/g).

Bn (Background) = the metals concentration (µg/g) in reference (background) environment.

Bref (background) = the reference metals concentration (µg/g) in reference background environment. According to Acevedo-Figueroa *et al.* (2006) six contamination categories are recognized on the basis of the enrichment factor:

<1 indicates no enrichment.

= 1-2 → minimal enrichment.

= 2-5 → moderate enrichment.

= 5-20 → significant Enrichment.

= 20-40 → very high enrichment.

> 40 → extremely high enrichment.

As the Enrichment factor increase, the contributions of the anthropogenic origins also increase (Sutherland, 2000). The commonly used reference metals are Mn, Al and Fe (Liu *et al.*, 2005), thus, Mn was used as

the reference metal in this study because it was found in abundant amount in the sediment and natural environment.

2.5.1.5 Potential Ecological Risk Index (E^i_f)

The potential ecological risk of a given contamination was calculated according to Hakanson (1980) and Kucuksezgin *et al*. (2008)

$$\mathbf{E^i_f = T^i_f .\ C^i_f}$$

$\mathbf{T^i_f}$ is the toxic response factor for a given heavy metal,

$\mathbf{C^i_f}$ is the contamination factor.

$\mathbf{T^i_f}$ for Cd and Zn are 30 and 1 respectively, (Hakanson, 1980). The potential ecological risk of heavy metals is classified into five levels according to the values of $\mathbf{E^i_f}$:

$< 20 \rightarrow$ low.

$= 20\text{-}40 \rightarrow$ moderate.

$= 40\text{-}80 \rightarrow$ considerable.

$= 80\text{-}160 \rightarrow$ high.

$> 160 \rightarrow$ very high.

2.5.2 Calculation of Bio-Accumulation Factor (BAF) and Bio-Sedimentation Factor (BSF)

The calculation of BAF and BSF for determine heavy metals that transfer among water, sediments, and biota were calculated according to Evans and Engel (1994)

$$\mathbf{BAF = [M_{tissue}] / [M_{water}]}$$

$$\mathbf{BSF = [M_{tissue}] / [M_{sediment}]}$$

M tissue = Metal concentration in soft tissue.

M water= Metal concentration in water.

M sediment = Metal concentration in sediment.

2.6 Blank solutions

Blank solution was prepared for each type of samples (water, sediment and fish) by treated in the same way of those digested of samples without samples.

2.7 Statistical analysis

The statistical analyses were performed by using SPSS software (Ozdamar, 2005). To demonstrate the significant differences between the months as well as the stations was used Duncan's multiple range test (Duncan, 1955). The mean and standard deviation were measured for each the previous variables. The correlation coefficient among parameters and dissolved heavy metals was calculated in the current study. The level of significance was set at $P<0.05$

Chapter three

Results and discussion

3.1 Heavy metals

3.1.1 Heavy metals (cadmium, zinc and manganese) in filtered water of Tigris River

Over the past century, heavy metals have been discharged into the world rivers and estuaries as a result of the rapid industrialization (Tam and Wong, 2000; Cobelo-Garćĺa and Prego, 2003; Chen *et al.,* 2004; Pekey, 2006). Iraq and other developing countries, where environmental protection laws have not been enforced, industrial and domestic wastes are dumped indiscriminately into water bodies. These wastes have been reported to contain toxic and hazardous substances including heavy metals. The pollution of water resources, sediment, soil and fish by heavy metals is an important concern because of their toxicity, persistence and bio-accumulative nature (Ikem *et al.,* 2003).

According to Mason (1991), heavy metal pollution is one of the five major types of toxic pollutants commonly present in surface waters. If they reach high enough levels, they may become toxic to aquatic organisms. Heavy metal concentrations in the environment are of great concern due to their serious effects through the food chain on animal and human health (Ma, 2005). A low amounts of heavy metals which found on fresh water and always released from erosion of soil and rocks (Al-Juboury, 2009; Babel and Opsio, 2007). Recently, the monitoring of water quality is very important in rivers that are affected by pollutants discharge from cities, atmospheric precipitation and industrial domestic sewage that represent the major source for water pollution (Lwanga *et al.,* 2003; Lomniczi *et al.,* 2007). The point sources of pollution in Iraq come in many forms such as of industrial effluents and domestic sewage (Al-Saadi *et al.* 1986).

3.1.1.1 Cadmium (Cd)

Cadmium is a toxic element, which occurs naturally in fish, sediment and water, and exists along with zinc in nature. It has no known essential biological function (Irwin *et al.,* 1997). Cadmium is generally present in the environment at low levels; however, human activity has greatly increased those levels (IPCS, 1992). It can travel for a long distances from the source of emission by atmospheric transport (WHO, 2007).

Results of present study showed that highest value of dissolved cadmium concentration 0.01 ppm was measured in February, April, and August 2012 at station 4, whereas the lowest value 0.0003 ppm was measured in December 2012 at station 4. The average of dissolved Cd concentration during this study was 0.004 ppm (Fig. 3; Table 4). Seasonally, the results of this study showed that the high values of dissolved Cd were found in spring, summer and later stage of winter months and the low values were observed during winter and autumn months. The statistical analysis of the data showed significant differences among stations ($P<0.05$) except between station 1 and station 2 (Table 4).

From results of this study, the concentrations of Cd were low that may be due to the Cd found in low quantities less than 0.001 mg/l in earth crust (Boyd, 2000).

The mean concentration of dissolved cadmium in the present study within the permissible limit for each Iraqi standards of river water (1967) No. (25), Iraqi standards for drinking water (1986), as well as WHO standards for drinking water (1984) and USEPA (1992). All these standards for Cd were 0.005 ppm. Beside these the mean concentration of Cd was within acceptable limit set by EPA (2002), as well as WHO standards for drinking water (2003), which were 0.01 ppm. While, the average of dissolved Cd was above WHO standards for drinking water (1996), WHO standards for drinking water

(2006), USEPA (2007) and WPCL (Water Pollution Control Legislation) (2004) that recommended permissible limit 0.003 mg/l (Table 5).

The concentration of dissolved cadmium found in this study considered high when compared with other studies such as Abaychi and DouAbul (1985) their study on the Shatt Al-Arab River; Al-Khafajii (1996) studied the concentrations of Cd on the Shatt Al-Arab Estuary, Rasheed *et al.* (2001) studied this concentrations in the Tigris River and Sabri *et al.* (2001) evaluated the Cd in Tigris River at Samarra, Al-Taee (1999) studied in Shatt Al-Hilla River, and Salman study (2006) on the Euphrates River between Al-Hindia dam and Al-Kufa region. But our study results considered low when compared with other study of Al-Saadi *et al.* (2000b) on the Diyala River. The Study of Kassim *et al.* (1997) recorded values for dissolved Cd varied between ND to 0.0016 ppm in Euphrates River, while the study of Fahad (2006) recorded the value of dissolved Cd reached to 0.0263 ppm in Al-Gharraf River.

The current results were less than the international study of Ekeanyanwu *et al.* (2010) on the Okumeshi River in Nigeria who found Cd concentration (0.03 ppm) and also less than the study of Aktar *et al.* (2011) on the Ganga River, who recorded the value for Cd reached to (0.03ppm). While, the present results were higher than results of Wang *et al.* (2010) on the Yellow River in China and another study by Papafilippaki *et al.* (2008) on the Keritis River in Chania, Greece, as well as study of Karadede-Akinand and Ünlü (2007) on Tigris River in Turkey. All these were summarized in Table 6. Generally, present values of Cd were nearly and sometime above Iraqi and world standards limits, which may be indicate to no pollution to slightly pollution of the river water.

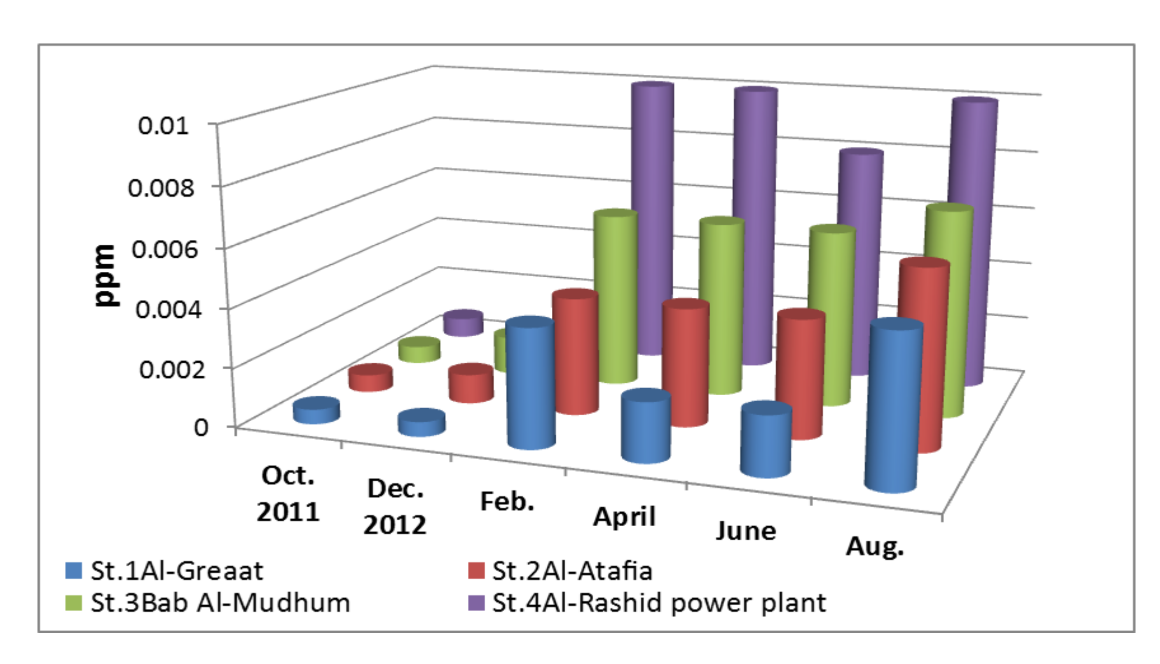


Figure (3): Variation of dissolved cadmium during the study period

Table (4): The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in filtered water of four studied stations

Dissolved metals (ppm)		S1	S2	S3	S4
Cd	**Min**	0.0005	0.0006	0.0006	0.0003
	Max	0.005	0.006	0.007	0.01
	Mean ±SD	0.0023 ±0.0019 **c**	0.0032 ±0.0020 **c**	0.0044 ±0.0026 **b**	0.0065 ±0.0051 **a**
Zn	**Min**	0.0015	0.003	0.0028	0.0035
	Max	0.04	0.06	0.06	0.1
	Mean ±SD	0.0156 ±0.0146 **b**	0.0205 ±0.0202 **b**	0.0223 ±0.02006 **b**	0.0355 ±0.0384 **a**
Mn	**Min**	0.0006	0.0007	0.0007	0.0008
	Max	0.11	0.012	0.018	0.022
	Mean ±SD	0.0047 ±0.00456 **c**	0.0056 ±0.004962 **c**	0.0076 ±0.007071 **b**	0.0104 ±0.008924 **a**

Different letters in same row that indicate for the different significance

Table (5): Compared studied elements (Cd, Zn, and Mn) in filtered water of Tigris River with local and international standards limits

The Iraqi and the World Standards	Cd ppm	Zn ppm	Mn ppm
Iraqi standards for river water (1967) No. 25	0.005	0.5	0.1
Iraqi standards for drinking water (1986)	0.005	1	0.1
USEPA (1976)	_	5	0.65
WHO standards for drinking water (1984)	0.005	0.5	0.1
USEPA (1992)	0.005	_	_
WHO standards for drinking water (1996)	0.003	_	0.5
EC (European Commission) (1998)	5	_	0.05
EPA (2002)	0.01	_	0.02
WHO standards for drinking water (2003)	0.01	_	0.5
WPCL (Water Pollution Control Legislation) (2004)	0.003	_	_
WHO standards for drinking water(2006)	0.003	_	_
USEPA (2007)	0.003	0.015	_
Present study	0.004	0.023	0.007

Table (6): Compared studied elements (Cd, Zn, and Mn) in filtered water of Tigris River with local and international studies

Metals (ppm) / Place	Cd	Zn	Mn	Reference
Shatt Al-Arab River, Iraq	0.00026	0.0018	0.0013	Abaychi and DouAbal (1985)
Shatt Al-Arab Estuary, Iraq	0.00019	0.00082	0.00152	Al-Khafajii (1996)
Tigris River, Iraq	ND-	0.0026-	0.003-	Kassim *et al.* (1997)

	0.0016	0.0556	0.0632	
Al-Hilla River Iraq	0.0011	0.00873	0.00096	Al-Taee (1999)
Diyala River, Iraq	0.025	1.13	0.043	Al-Saadi *et al.* (2000b)
Tigris River, Iraq	ND-0.0027	0.000001-0.0297	ND-0.0095	Rasheed *et al.* (2001)
Tigris River, Iraq	ND-0.0006	0.007-0.01	_	Sabri *et al.* (2001)
Upper-mid region of Tigris River, Iraq	0.0002-0.0037	0.0262-0.1521	0.015-0.109	Al-Lami and Al-Jaberi (2002)
Al-Gharraf s. sector	0.0263	0.01718	_	Fahad (2006)
Euphrates River Iraq	0.00214	0.0105	0.00612	Salman (2006)
Tigris River, Iraq	0.0000135	_	_	Hashim (2010)
Al-Gharraf River, South of Iraq	0.00034	0.0366	_	Al-Helaly (2010)
Tigris River, Iraq	_	0.0016-0.0743	_	Ahmed (2012)
Tigris River, Iraq	_	0.0313	_	Mustafa (2012)
Warri River, Nigeria	0 - 0.39	_	_	Ayenimo *et al.* (2005)
Tigris River, Turkey	ND-ND	0.00007-0.00013	ND-ND	Karadede-Akinand and Ünlü (2007)
Ganga River, west Bengal	0.001-0.003	0.012-0.37	0.025-2.72	Kar *et al.* (2008)
Gediz River, Eastern Aegean	_	0.00019-0.0029	0.03-0.17	Kucuksezgin *et al.* (2008)
Keritis River, Chania, Greece	0.000005-0.000019	0.004-0.039	_	Papafilippaki *et al.* (2008)
Ganges River, India	0.008	0.072	_	Gupta *et al.* (2009)
Okumeshi River, Nigeria	0.03	_	0.13	Ekeanyanwu *et al.* (2010)

Khoshk River, Shiraz, Iran	0.001	1.4	0.28	Salati and Moore (2010)
Yellow River, China	0.00045	0.0083	_	Wang *et al.* (2010)
Ganga River, India	0.03	0.29	_	Aktar *et al.* (2011)
Tigris River	0.004	0.023	0.007	Present study

*ND: Not Detected

3.1.1.2 Zinc (Zn)

Zinc is an essential element for aquatic life, high concentration of this metal may exceed this requirement and the detoxification mechanisms for the animal may be insufficient to cope with the influx, the zinc will then exert a direct toxic action (Lloyd, 1992). It being involved in nucleic acid synthesis and occurs in many enzymes. Zinc occurs in to oxidative states in aquatic ecosystems, namely as a metal, and as zinc (II) ions. In aquatic ecosystem the zinc (II) ion is toxic to fish and aquatic organisms at relatively low concentrations. Soluble zinc salts (for example, zinc carbonate, zinc oxide and zinc sulphade) occurs readily industrial wastes (DWAF, 1996). Zinc occurs in nature together with other metals of which iron and cadmium in most common (Dallas and Day, 1993).

Dissolved zinc concentrations of all stations are shown in Fig. 4; Table 4. The highest value of dissolved zinc concentration 0.1 ppm has been noted at station 4 in April 2012, while the lowest concentration value 0.0015 ppm was recorded at station 1 in December 2012. The annual average of Zn concentration was 0.023 ppm. Seasonally, the high values of dissolved zinc were recorded during spring months while the low values were observed in winter and autumn months. The statistical analysis of the data showed no significant differences was found among stations ($P<0.05$) except station 4 (Table 4).

From results of this study, the concentrations of Zn were high values may be due to the effects of discharge of industrial effluents compounds

including heavy metals into natural fresh water bodies without prior treatment such as textile factory, dyes factories and effects of the trocar (Al-Maliky, 2005). Moreover, the domestic sewage added more amount of zinc (Alloway and Ayres, 1997; APHA, 1998).

In present study, the average concentration of dissolved Zn was within the safe limits of Iraqi and the world standards that were mentioned in this study in Table 5. While, the mean concentration of Zn was above the USEPA (2007) recommended maximum values 0.015 ppm.

The concentration of dissolved zinc found in this study considered relatively high when compared with study of Al-Khafajii (1996) on the Shatt Al-Arab and Rasheed *et al.* (2001) who studied concentrations of zinc in the Tigris River. Concentrations of dissolved zinc in Tigris River were higher than the concentrations of zinc in other studies (Sabri *et al.,* 2001; Salman, 2006). But another study of Al-Saadi *et al.* (2000b) on the Diyala River showed that the mean concentration of zinc was higher than results of this study. Dissolved zinc of this study considered low when compared with study of Al-Lami and Al-Jaberi (2002) they studied the concentration of zinc in upper region of Tigris River. Another study of Kassim *et al.* (1997) on Euphrates River recorded the concentration values of dissolved Zn varied between 0.0026 to 0.0556 ppm, while in Al-Gharraf River, Fahad (2006) recorded the dissolved Zn was 0.0171 ppm and in the Ganga River in India, Aktar *et al.* (2011) recorded the Zn concentration reached to 0.29 ppm.

While, the results of Zn in current study was higher than the results of the study of Wang *et al.* (2010) on the Yellow River in China and also study of Papafilippaki *et al.* (2008) on the Keritis River in Chania in Greece, as well as another study by Karadede-Akinand and Ünlü **(**2007) on Tigris River in Turkey (Table 6).

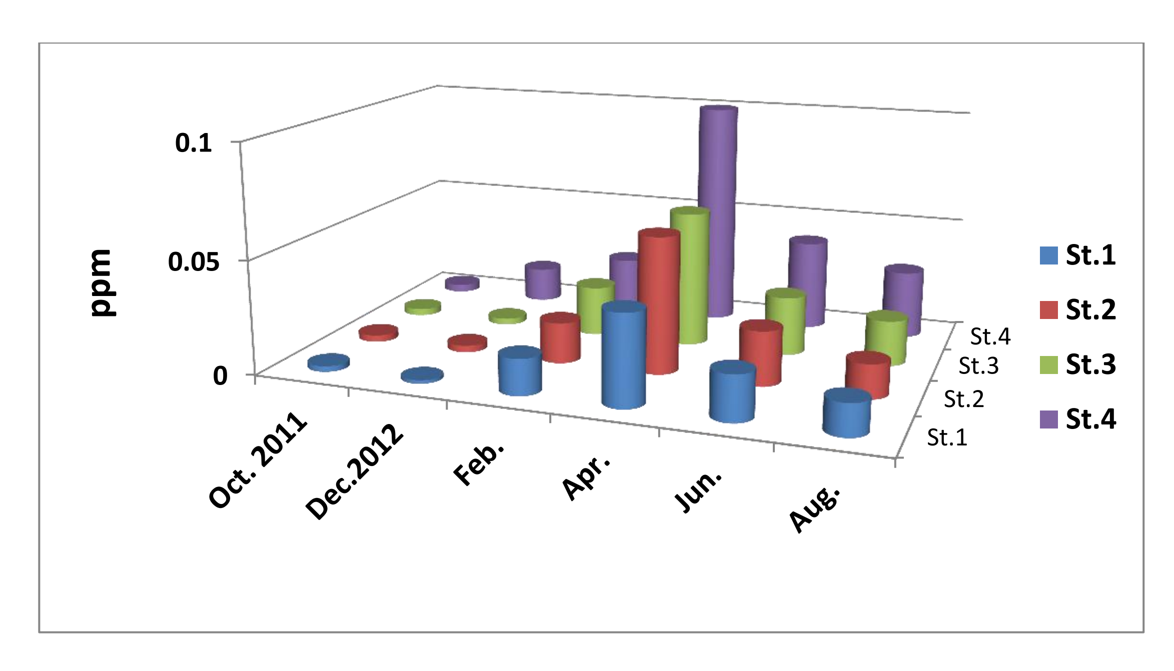


Figure (4): Variation of dissolved zinc during the study period

3.1.1.3 Manganese (Mn)

Manganese one of priority micronutrient which required for aquatic organisms and it have important role due to it is enzyme catalysis (Al-Saadi, 2006a, b). It found in igneous basal rocks and acidic rocks and was found in sedimentary rocks and the concentrations of Mn increase in sediment, which has the small sizes of molecules such as clay (Pinta and Ollat, 1961). When, the concentration of Mn increase more than 0.1 ppm that leads to influence on growth of organisms (Waite, 1984). The concentration of dissolved manganese is influenced by changes in redox potential, dissolved oxygen, pH and organic matter (Anon, 1996). Manganese is a naturally occurring element in the environment. In the nature is found in form of oxides, silicates, and carbonates etc. (NAS, 1973).

The results of this study showed that the highest value of dissolved manganese concentration 0.022 ppm recorded at station 4 in February 2012, while the lowest value 0.0006 ppm recorded at station 1 in October 2012. The annual average of Mn was 0.007 ppm (Fig. 5; Table 4). Seasonally, the high values of dissolved Mn were observed during later stage of winter and summer months, whereas the low values were found in autumn months and

first stage of winter months. The statistical analysis of the data showed significant differences among stations ($P<0.05$) except between station 1 and station 2 (Table 4).

In present study the average concentration of dissolved Mn was within the safe limits of Iraqi specifications and the world standards that was mentioned in this study which shown in Table 5.

The concentration of dissolved manganese found in this study was higher than other studies (Abaychi and DouAbul, 1985; Al-Khafajii, 1996; Rasheed *et al.,* 2001; Al-Taee, 1999 and Salman, 2006). But study of Al-Saadi *et al*. (2000b) on the Diyala River showed the concentration of Mn was higher than results of current study. Al-Lami and Al-Jaberi (2002) recorded that the values of dissolved manganese on the upper region of Tigris River higher than this study. Another study on the Euphrates River by Kassim *et al.* (1997) recorded the concentration values of dissolved Mn were ranged from 0.003 to 0.0632 ppm.

The present results of Mn were less than the results of Ekeanyanwu *et al.* (2010) on the Okumeshi River in Nigeria who found Mn concentration (0.13 ppm), while the results of Mn in this study were higher than results of Wang *et al.* (2010) they worked in the Yellow River in China and also higher than study of Karadede-Akinand and Ünlü in Tigris River in Turkey (2007) (Table 6).

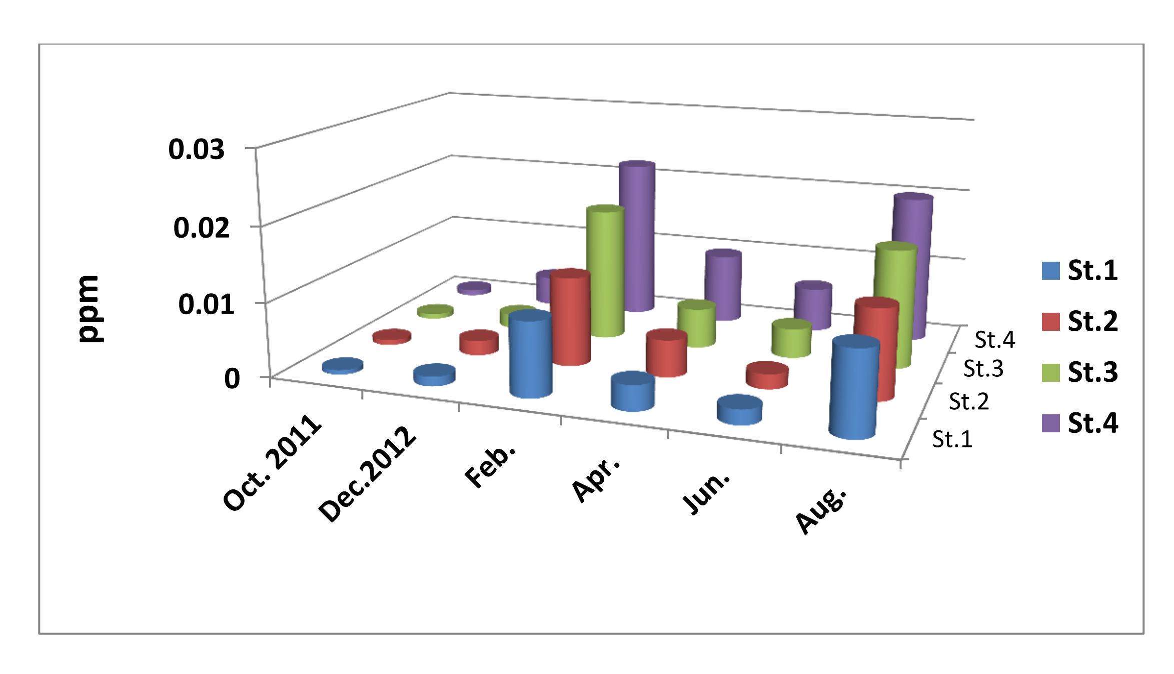


Figure (5): Variation of dissolved manganese during the study period

There were some spatial variations in concentrations of studied heavy metals among different stations which may due to the distribution of elements are affected by many important spatial factors such as, human population, density along the riverbanks, hydrological conditions of the bed, discharges by local industries, and sewage discharges (Draskovic and Draskovic, 1980). In comparison to stagnant waters, running water is a particularly complex situation for rivers; alter not only through cyclic, seasonal progressions, but also along their lengths, according to their depth, gradient rate of flow, geology, salt concentration, turbidity etc. Thus there is a multitude of biological habitats (Javed, 2005); also there were clear seasonal variations in concentrations of the studied heavy metals. Considerable variations in the heavy metals were observed in all the samples studied with minimum accumulation of studied heavy metals during autumn and winter months while the maximum accumulation during spring and summer. It has been observed that changes in pH, temperature, water hardness, dissolved oxygen, rain fall, climatic changes etc, all affect on the presence of heavy metals in aquatic environment (Eggleton and Thomas, 2004). For this study the concentrations

of dissolved zinc in Tigris River were higher than the concentrations of dissolved cadmium and manganese, and the order was Zn> Mn > Cd.

During the rainy season rivers are heavily flooded and the drainage system is drastically affected which results in mixing of polluted and unpolluted water, this leads to decrease in heavy metal concentration (Collvin, 1985). Whereas, increase in the concentration of metals during summer seasons could be due to drought and decrease in water level.

3.1.2 Heavy metals in sediments of Tigris River

Sediments are important hosts for pollutants like heavy metals; therefore, it has been employed to monitor the pollution in aquatic environments (Saloman *et al.*, 1987). Since sediments act as sinks for contaminants, which can persist in the aquatic environment for decades, changes in sediment in fauna activity and water chemistry allow these persistent contaminants to enter food chain, and thus into fish tissues (Kirby *et al.*, 2001). For this reason, the sediments reflect the history of water body pollution (Jain, 2004).

3.1.2.1 Cadmium (Cd)

The present results showed that the highest concentration of Cd in sediments was 2.5 ppm at station 4 in October 2011, and the lowest concentration 0.5 ppm at station 1 and 2 in December and station 1 in February 2012. The annual mean was 1.38 ppm (Fig. 6; Table 7).

Seasonally, the low concentrations of Cd were observed during winter and spring months, whereas the high concentrations of Cd were in autumn and summer months. The statistical analysis of the data showed significant differences among months, also there was a significant differences among stations ($P<0.05$) (Table 7).

Present study showed the mean concentration of cadmium in sediments is above the ERL (Effects Range Low value) of NOAA (National Oceanic and Atmospheric Administration) (1990) cited in Long and Morgan (1990), LEL (Lowest Element Level) and TEL (Threshold Element Level) of NOAA(

2009) which were 1.2 ppm, 0.60 ppm and 0.99 ppm, respectively, The mean concentration of cadmium is a lower than the concentrations in EPA (Environmental Protection Agency) (1976), ERM (Effects Range Medium value) of NOAA(1990), PEC (Probable Effect Concentration) and SEC (Sever Effect Concentration) of NOAA(2009), which were 2 ppm, 9.6 ppm, 4.90 ppm and 10.0 ppm, respectively (Table 8).

The concentrations of cadmium considered high as compared with previous studies (Abaychi and DouAbul, 1985; Abaychi and Mustafa, 1988 on the Shatt Al-Arab River; Al-Khafaji (1996); Sabri *et al.* (2001); Al-Lami and Al- Jaberi (2002); Rabee *et al.* (2011) on the Tigris sediments in Baghdad region and Rabee *et al.* (2009) on the sediments of Tigris and Euphrates Rivers). In Al-Hilla River, Al-Taee (1999) recorded value of Cd reached to 3.92 ppm. The concentration of Cd in sediments of this study was higher than other international studies such as Salati and Moore (2010) study on the Khoshk River in Shiraz at Southwest of Iran, and Wang *et al.* (2010) on the Yellow River in China, in addition to another study by Gupta *et al.* (2009) on the Ganges River at Allahabad in India (Table 9).

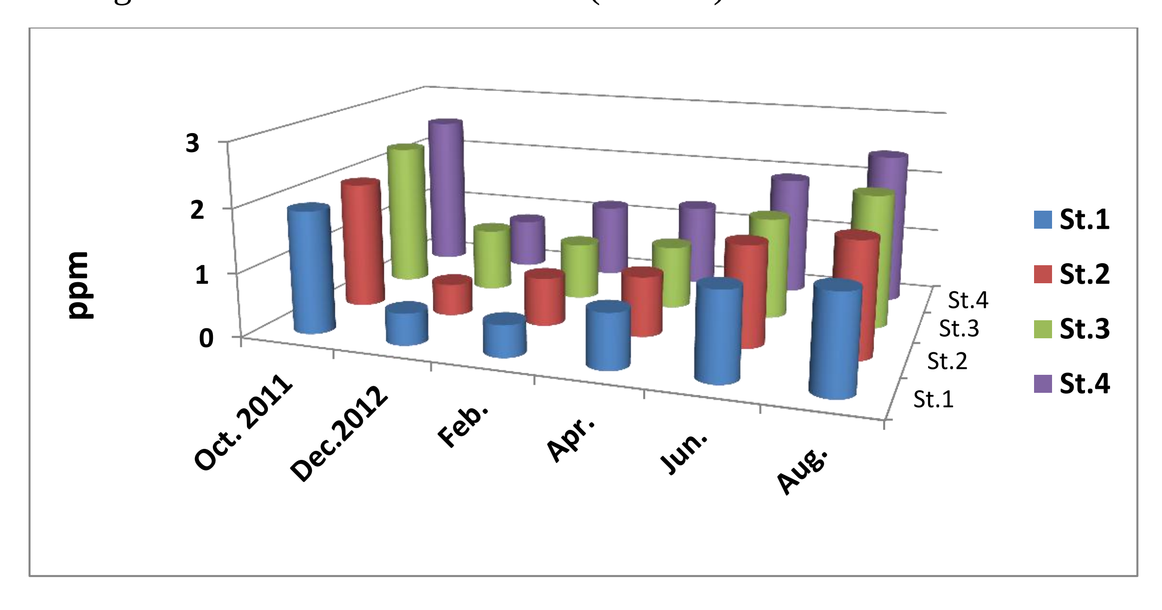


Figure (6): Variation of cadmium in sediments during the study period

Table (7): The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in the river sediments of four studied stations

Metals in sediments (ppm)		S1	S2	S3	S4
Cd	Min	0.5	0.5	0.9	0.8
	Max	1.92	2	2.3	2.5
	Mean ±SD	1.1066 ±0.5625 **d**	1.2633 ±0.5845 **c**	1.4833 ±0.5893 **b**	1.6744 ±0.6731 **a**
Zn	Min	51.2	51.5	65.2	60.5
	Max	160	137	170	188
	Mean ±SD	77.7166 ±39.1472 **c**	74.8 ±29.5455 **c**	88.8333 ±38.1588 **b**	103 ±42.1747 **a**
Mn	Min	73.7	85.6	79	85
	Max	465	460	470	490
	Mean ±SD	226.58 ±174.3019 **b**	228.28 ±167.8385 **b**	241.37 ±172.9666 **a**	237.95 ±177.961 **a**

Different letters in same row that indicate for the different significance

Table (8): Compared studied elements (Cd, Zn, and Mn) in sediments of Tigris River with international standards

World Standards	Cd ppm	Zn ppm	Mn ppm
EPA (1976)	2	40	_
ERL (Effects Range Low value) NOAA (1990)	1.2	150	_
ERM (Effects Range Medium value) NOAA (1990)	9.6	410	_
LEL (Lowest Element Level) NOAA (2009)	0.60	_	_
TEL(Threshold Element Level) NOAA (2009)	0.99	_	_
PEC (Probable Effect Concentration) NOAA (2009)	4.90	_	_
SEC (Sever Effect Concentration) NOAA (2009)	10.0	_	_
Present study	1.38	86	231.4

Table (9): Compared studied elements (Cd, Zn, and Mn) in sediments of Tigris River with local and international studies

Metals (ppm) / Place	Cd	Zn	Mn	Reference
Shatt Al-Arab River, Iraq	0.18	34.70	642.0	Abaychi and DouAbal (1985)
Shatt Al-Arab River, Iraq	0.03	5.80	914.0	Abaychi and Mustafa (1988)
Shatt Al-Arab Estuary, Iraq	0.27	31.99	404.1	Al-Khafagi (1996)
Tigris River, Iraq	_	25.87	209.6	Al-Lami (2002)
Euphrates River, Iraq	11.22	67.66	37.7	Salman (2006)
Tigris River, Iraq	0.45-0.625	43.5-57.5	_	Sabri *et al.* (2001)
Upper-mid region of Tigris River, Iraq	0.06-1.90	6.25-69	270-710	Al-Lami and Al-Jaberi (2002)
Tigris River, Iraq	0.4-1.35	24.8-85	301-730	Rasheed *et al.* (2001)
Al-Hilla River, Iraq	3.92	73.41	239.07	Al-Taee (1999)
Tigris River, Iraq	1.28	_	442.3	Rabee *et al.* (2009)
Euphrates River, Iraq	0.73	_	302.7	Rabee *et al.* (2009)
Tigris River, Iraq	0.095	_	_	Hashim (2010)
Tigris River, Iraq	0.73	_	265.2	Rabee *et al.* (2011)
Tigris River, Iraq	_	83.35	_	Ahmed (2012)
Weihei River, Shaanxi	0.05-0.17	30.98-177.38	_	Hua *et al.* (2011)
Second Songhua River, China	_	21.8-403.1	_	Lin *et al.* (2008)
Khoshk River, Shiraz, Iran	1.23	64.81	231.46	Salati and moore (2010)
Yellow River, China	0.586	78.531	_	Wang *et al.* (2010)
Ganges River, India	0.86	14.62	_	Gupta *et al.* (2009)

Okumeshi River, Nigeria	1.32	_	2.76	Ekeanyanwu *et al.* (2010)
Ganga River, India	40.16	60.08	_	Aktar *et al.* (2011)
Tigris River	1.38	86	231.4	Present study

3.1.2.2 Zinc (Zn)

In present study the concentration of Zn was measured in sediments. The maximum concentration of Zn was 188 ppm in station 4 in December 2012, while the minimum concentration was 51.2 ppm in station 1 in June 2012. The annual average was 86 ppm (Fig. 7; Table 7).

Seasonally, the high concentrations have been noted during winter months, while the low values were recorded during summer and spring months. The statistical analysis of the data showed significant differences among the concentration of Zn in all months except October with each of February and August and there was a significant differences was found among all stations (P<0.05) except between station 1 and station 2 (Table 7).

The maximum value and the mean value of zinc exceed the permissible limit (40 ppm) according to EPA (1976), while the mean value of zinc measured within acceptable limits set by ERL, and ERM of NOAA (1990) (Table 8). In current study, the concentrations of zinc in sediments were considered high when compared with other studies on the Tigris River (Al-Lami, 2002), on the Euphrates River (Salman, 2006), on the Shatt Al-Arab River (Abaychi and DouAbul , 1985; Abaychi and Mustafa, 1988), on the Shatt Al-Arab of Arabian Gulf (Al-Khafaji ,1996), on the Tigris River at Samarra impoundment (Sabri *et al*., 2001), on the upper-mid region of Tigris (Al-Lami and Al- Jaberi, 2002), on the Tigris River sediments in Baghdad region (Rabee *et al.*, 2011), and the study on the sediments of Tigris and Euphrates Rivers (Rabee *et al.*, 2009). Whereas, Al-Taee (1999) studied the concentration of Zn in Al-Hilla River, she reported that concentration of Zn

reached to 73.41 ppm. In present study the concentration of Zn in sediments was higher than the results of another study of Salati and Moore (2010); they worked on the Khoshk River at Shiraz in Iran and also the study of Wang *et al*. (2010) on the Yellow River in China. Moreover, the similar finding was observed by Gupta *et al.* (2009) in the Ganges River at Allahabad in India. The concentration of Zn in present study was lower than its concentration in sediments of the Second Songhua River in China (Lin *et al.*, 2008) and in the sediments of Weihe River (Hua *et al.*, 2011) (Table 9).

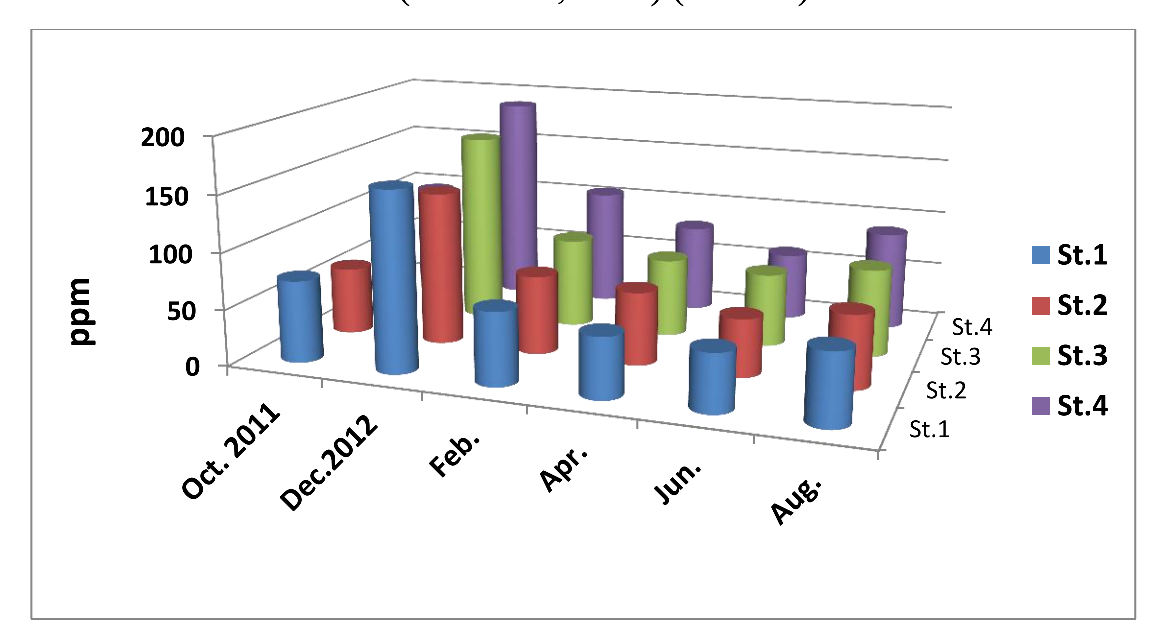


Figure (7): Variation of zinc in sediments during the study period

3.1.2.3 Manganese (Mn)

The results of sediments showed the maximum concentration of Mn was 490 ppm recorded at station 4 in Oct. 2011, while the minimum concentration (73.7 ppm) was recorded at station 1 in Apr. 2012. The annual mean of Mn was 231.4 ppm (Fig. 8; Table 7).

Seasonally, the high concentrations were recorded during the autumn and later stage of summer months, while the low concentrations were found during winter and spring months. The statistical analysis of the data showed significant differences among stations ($P<0.05$) except between station 1 and station 2, and between station 4 and station 3 (Table 7).

The concentrations of manganese found in sediments in this study was higher than other studies on the Tigris River (Al-Lami, 2002), on the Euphrates River (Salman, 2006). The concentrations of manganese considered low when compared with other studies on the Shatt Al-Arab River (Abaychi and DouAbul, 1985; Abaychi and Mustafa, 1988), on Shatt Al-Arab of Arabian (Al-Khafaji, 1996), on Tigris River at Samarra (Sabri *et al.*, 2001), on the upper-mid region of Tigris River (Al-Lami and Al-Jaberi, 2002), on Tigris River sediments in Baghdad region (Rabee *et al.*, 2011), and on the sediments of Tigris and Euphrates Rivers (Rabee *et al.*, 2009). However, the concentration of Mn in sediments in this study was higher than another study on the Khoshk River at Shiraz in Iran (Salati and Moore, 2010) (Table 9).

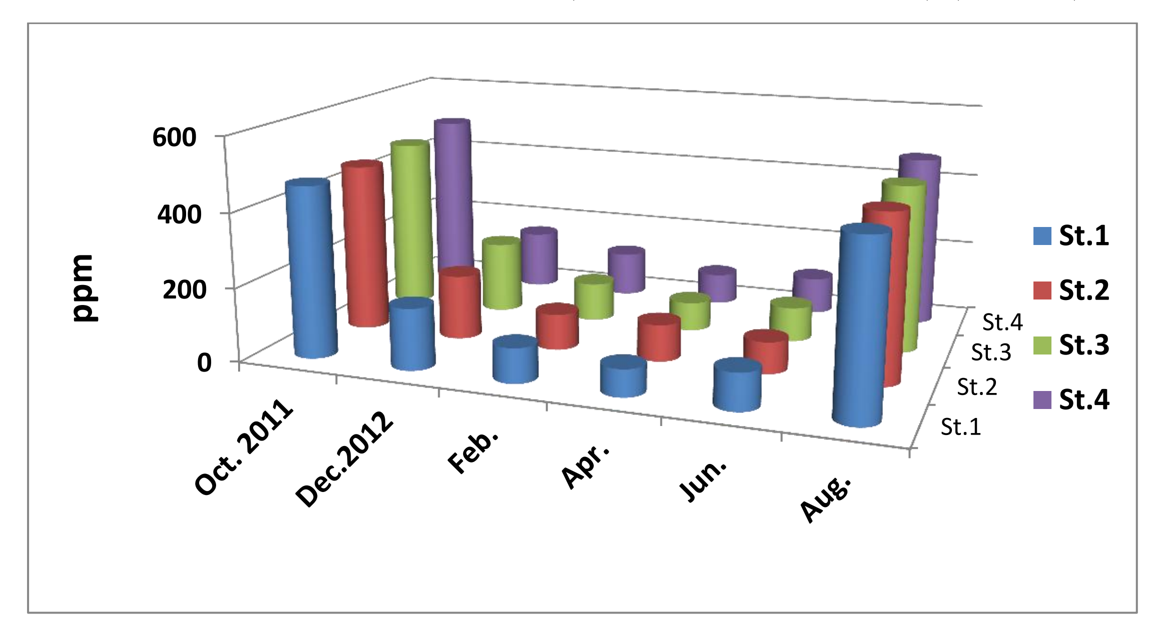


Figure (8): Variation of manganese in sediments during the study period

Sediments play an important role in the adsorption of dissolved heavy metals, which can also be a potential reservoir of metals, by releasing metal to the column of water under changing physical and chemical conditions. The concentrations of metals in sediment increased in southern stations inside Baghdad area especially in the station 4, this may be attributed to the increase of industrial activities in this region.

The comparison of metals concentrations in sediment between high and low discharges period, showed that the concentrations were high in low discharge (except Zn), and this may be due to the dilution factor related to the high discharge in winter and spring (Rasheed *et al.,* 2001). Almost, lower values of Cd and Mn were recorded during winter and spring, which may be due to the dilution effect during high water discharge.

The concentrations of heavy metals in sediments are varied according to the rate of particle sedimentation, rate of heavy metals deposition, the particle size and the presence or absence of organic matter (Saloman *et al.,* 1987). In general, metal concentration in the sediment increases with the decrease of organic matter content (Halcrow *et al.,* 1973). Heavy metals occur naturally in silt and clay-bearing minerals of terrestrial and marine geological deposits. The natural occurrence of heavy metals complicates the assessment of potentially contaminated estuarine sediments (Zhou *et al.,* 2004).

Metals enter into a number of reactions, including complication, precipitation and sorption, in the environment. These reactions affect their mobility and bioavailability standards for water quality have not yet included speciation of metals although the effect of complication to reduce metal toxicity is well known (Liu *et al.,* 2009). Gessey *et al.* (1984) stated that heavy metals react readily with suspended particulate matters and through sedimentation processes, accumulate in bottom deposits. Metals tend to accumulate in sediments from where they may be released and moving up through the food chain (Nabawi *et al.,* 1987).

The major source for the metal contamination in rivers is the industrial effluents near this rivers, as well as the transport of small fraction of sediment downstream due to the river velocity contributes to the accumulation of heavy metals in lower parts (Wakida *et al.,* 2008). Contaminated sediment can cause decrease in the ecosystem biodiversity and affects the aquatic system's food chain (USEPA, 2001). Trace metal contamination in sediment can affect on

the water quality and the bioaccumulation of metals in aquatic organisms, resulting in potential long-term implications on human health and ecosystem (Fernandes *et al.*, 2008).

The pollutants accumulated in sediments can return to waters in suspended or dissolved form. Therefore, they represent a potential risk for an aquatic environment and any water study ought to include an analysis of the sediment water comes into contact with (Enguix-González *et al.*, 2000).

3.1.3 Heavy metals in *Barbus xanthopterus*

Fish are the major part of the human diet and it is not surprising that numerous studies have been carried out on metal accumulation in different fish species (Kucuksezgin *et al.*, 2001). Fishes have been used for many years to indicate whether water is clean or polluted. Fishes are excellent biological markers of metals in waters (Rashed, 2001).

3.1.3.1 Cadmium (Cd)

The contaminations with Cd varied among organs, seasons, and locations. The results of this study showed that maximum concentration of cadmium (0.079 ppm) which was recorded in gills of fish collected from station 4 in April 2012, while the minimum concentration 0.0001 ppm was in intestine of fish collected from station 4 in February 2012. The highest annual average of cadmium concentration 0.012 ppm was recorded in gills, whereas the lowest average 0.004 ppm was in muscles (Fig. 9, 10 and 11; Table 10, 11 and 12).

Seasonally, the high concentrations of Cd were recorded in autumn, spring and summer months, while the low concentrations were in winter months. Locational, the concentrations of Cd were highest in fish collected from station 1 and lowest in fish collected from station 4. There was a significant differences was found between fish collected from stations for each muscles and intestine, while no significant differences between fish collected from station 1 and station 4 for gills ($P<0.05$) (Table 10, 11 and 12).

In present study, the maximum value of cadmium in fish within permissible limits of UNEP (1985), FAO (Food and Agriculture Organization) (1983), WHO (1993), as well as NSMD (National Standards Management Department) (2001) and IAEA-407 (International Atomic Energy Agency) (2005) cited in Wyse *et al.* (2005), while the maximum of cadmium is above safe limit of FEPA (Federal Environment Protection Agency) (1991) and EC (European Commission) (2005) (Table 13).

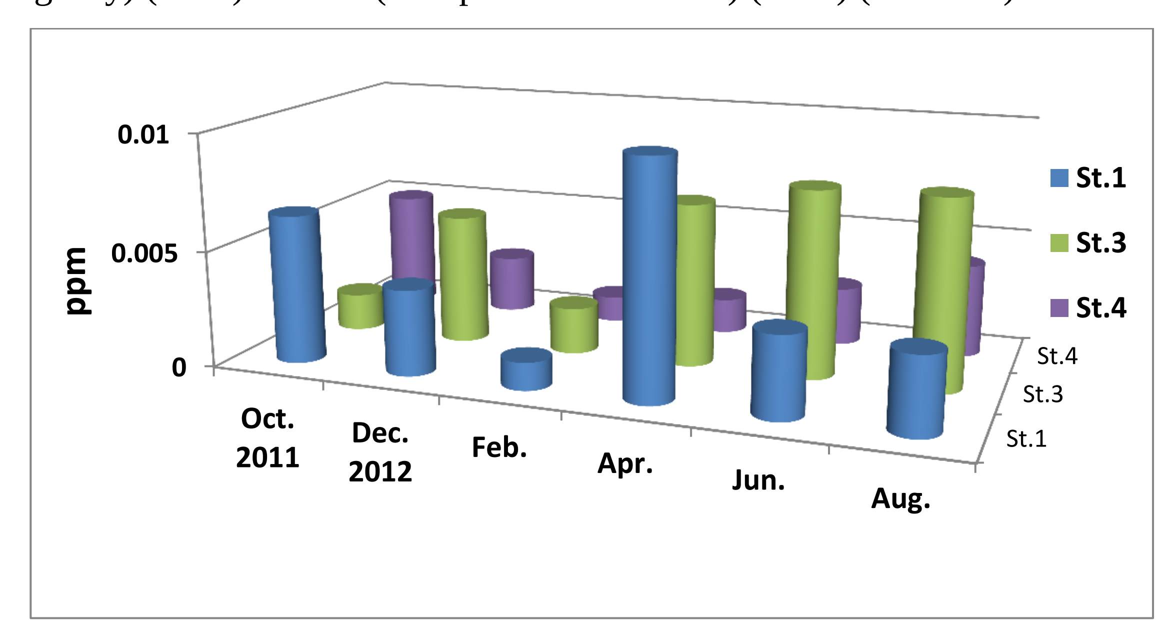


Figure (9): Variation of cadmium in muscles of fish (*B. xanthopterus*) that collected during the study period

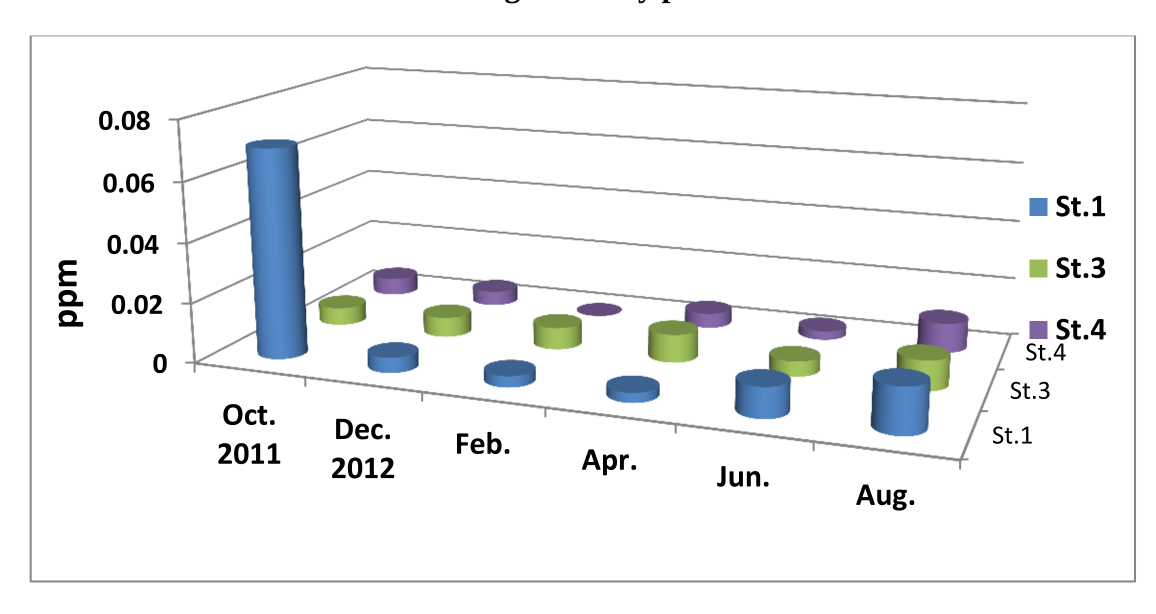


Figure (10): Variation of cadmium in intestine of fish (*B. xanthopterus*) that collected during the study period

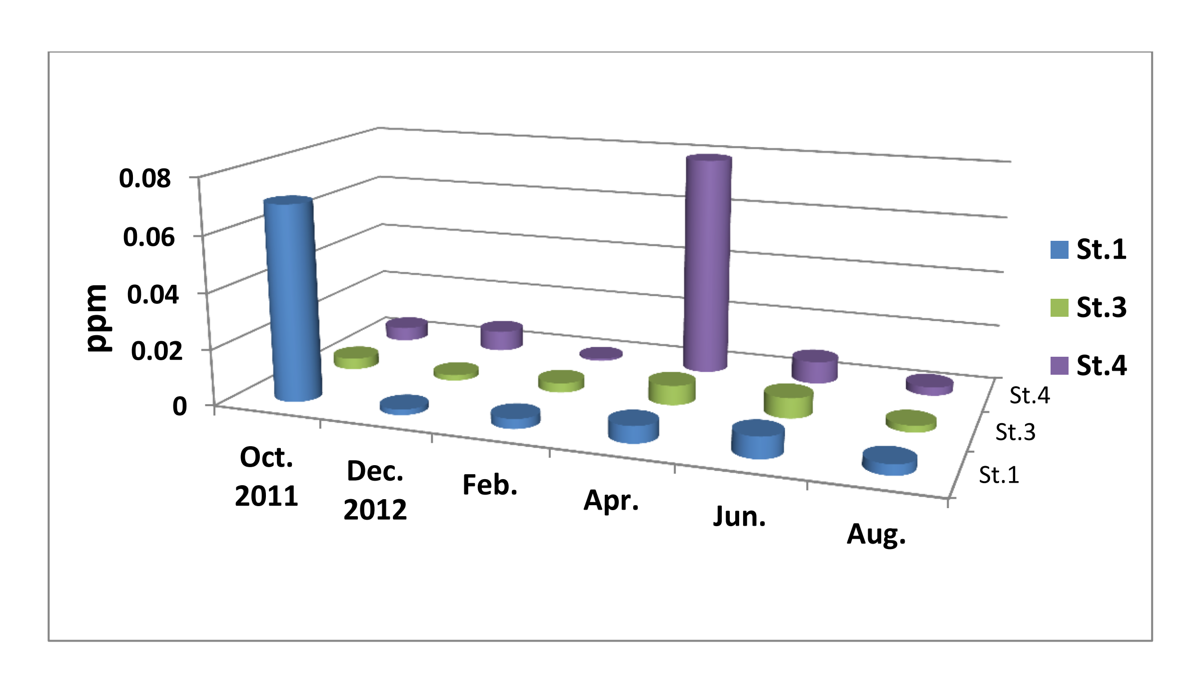


Figure (11): Variation of cadmium in gills of fish (*B. xanthopterus*) that collected during the study period

Table (10): The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in muscles of fish (*B. xanthopterus*) that collected from studied stations

Metals in muscles (ppm)		S1	S2	S3	S4
Cd	Min	0.0012	_	0.0016	0.0011
	Max	0.01	_	0.0081	0.005
	Mean ±SD	0.0046 ±0.00311 **b**	_ _	0.0053 ±0.0028 **a**	0.0027 ±0.0014 **c**
Zn	Min	0.0011	_	0.0015	0.0014
	Max	0.0048	_	0.0036	0.0035
	Mean ±SD	0.003 ±0.00123 **a**	_ _	0.0020 ±0.00084 **b**	0.0019 ±0.00075 **b**
Mn	Min	0.0091	_	0.0041	0.0058
	Max	0.069	_	0.077	0.066
	Mean ±SD	0.0365 ±0.02092 **a**	_ _	0.0289 ±0.023835 **c**	0.0296 ±0.02164 **b**

Different letters in same row that indicate for the different significances

Table (11): The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in intestine of fish (*B. xanthopterus*) that collected from studied stations

Metals in intestine (ppm)		S1	S2	S3	S4
Cd	**Min**	0.0032	_	0.005	0.0001
	Max	0.07	_	0.01	0.01
	Mean ±SD	0.0170 ±0.025058 **a**	_ _	0.0074 ±0.002892 **b**	0.0048 ±0.00376 **c**
Zn	**Min**	0.0016	_	0.0008	0.0016
	Max	0.006	_	0.004	0.005
	Mean ±SD	0.0027 ±0.001748 **a**	_ _	0.00188 ±0.001145 **b**	0.00236 ±0.001449 **ab**
Mn	**Min**	0.0095	_	0.0066	0.0072
	Max	0.09	_	0.056	0.0338
	Mean ±SD	0.0425 ±0.029401 **a**	_ _	0.02626 ±0.016366 **b**	0.02009 ±0.009817 **c**

Different letters in same row that indicate for the different significances

Table (12): The concentrations (Mean±SD) of different heavy metals studied (Cd, Zn, and Mn) in gills of fish (*B. xanthopterus*) that collected from studied stations

Metals in gills (ppm)		S1	S2	S3	S4
Cd	**Min**	0.002	_	0.002	0.0008
	Max	0.07	_	0.0072	0.079
	Mean ±SD	0.0154 ±0.025412 **a**	_ _	0.0043 ±0.002238 **b**	0.0172 ±0.02929 **a**
Zn	**Min**	0.002	_	0.002	0.0017
	Max	0.005	_	0.003	0.005
	Mean ±SD	0.0048 ±0.008865 **a**	_ _	0.0024 ±0.000813 **a**	0.0028 ±0.001459 **a**
Mn	**Min**	0.007	_	0.008	0.01
	Max	1	_	0.08	0.075
	Mean ±SD	0.1915	_ _	0.0393	0.0357

		±0.379048 **a**		±0.029697 **b**	±0.025869 **b**

Different letters in same row that indicate for the different significances

3.1.3.2 Zinc (Zn)

The maximum concentration of zinc 0.006 ppm was observed in intestine of fish collected from station 1 in October 2011, while the minimum concentration of Zn 0.0008 ppm was also found in intestine of fish collected from station 3 in December 2012. The highest annual average of zinc concentration (0.008 ppm) was found in gills, followed by the muscles and intestine (0.0023 ppm) (Fig. 12, 13 and 14; Table 10, 11 and 12). In general, the trend of heavy metals concentrations in various organs of the fish were used in this study and represented as follows: gills **>** muscles and intestine.

Seasonally, the high concentrations of Zn were found in autumn and the low concentrations in winter. Locational, fish that collected from station 1 and 4 was recorded as the highest concentrations of Zn, while fish that collected from station 3 was as the lowest concentrations. The statistical analysis of the data showed no significant differences was found between fish that collected from stations for gills and no significant differences except fish that collected from station 1 for muscles and between fish that collected from station 1 and station 3 for intestine ($P<0.05$) (Table 10, 11 and 12).

The maximum values of zinc within permissible limit of FAO (1983) and WHO (1993) (Table 13).

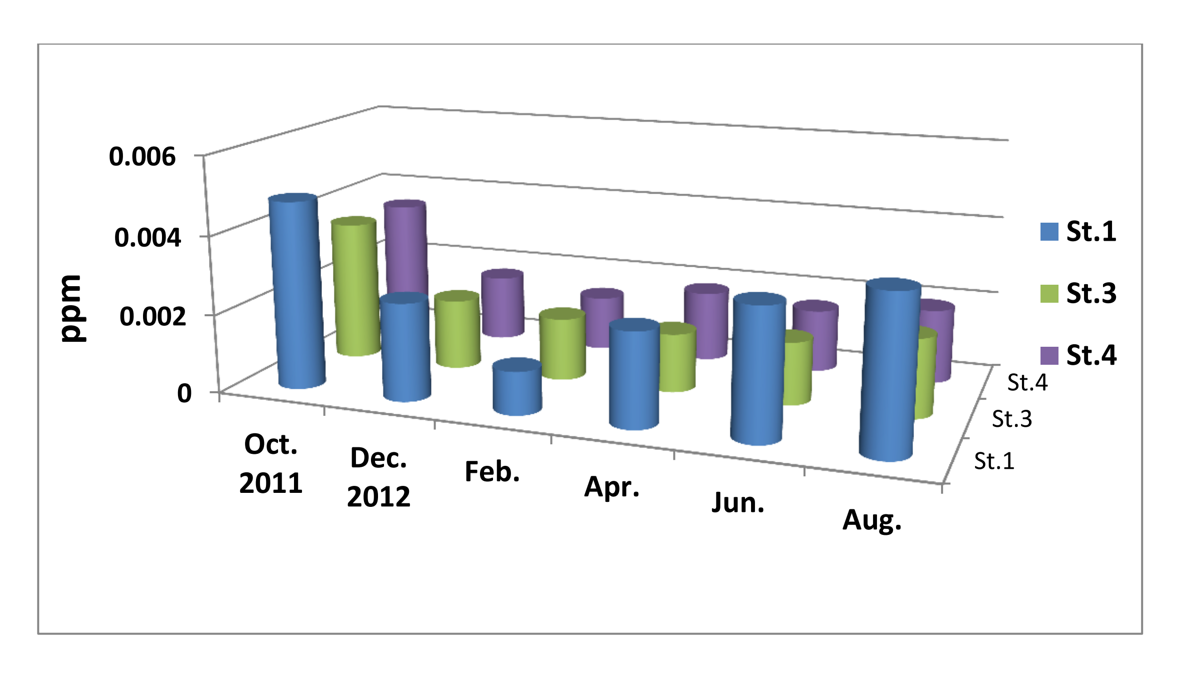


Figure (12): Variation of zinc in muscles of fish (*B. xanthopterus*) that collected during the study period

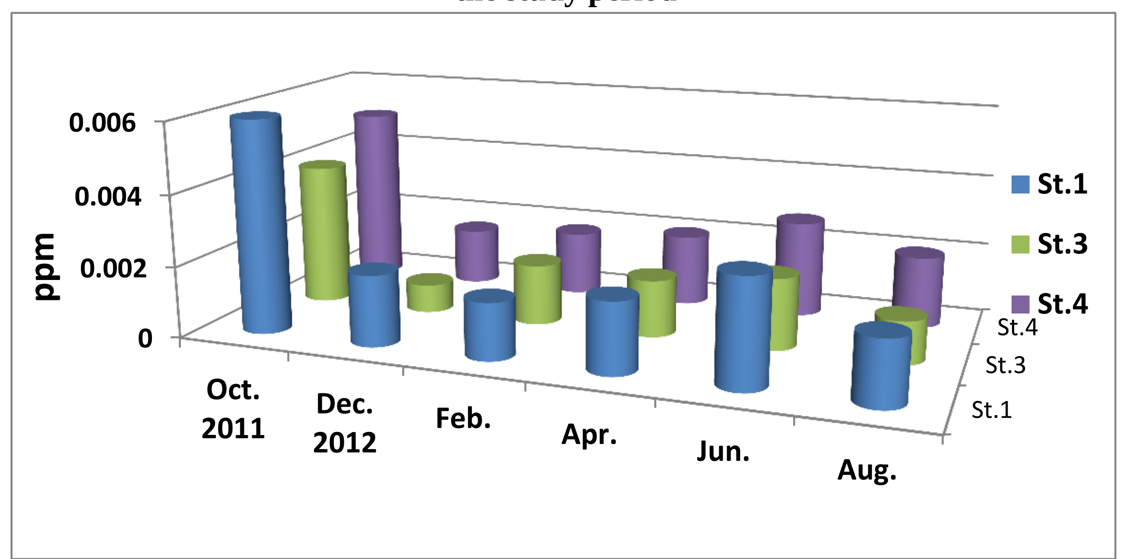


Figure (13): Variation of zinc in intestine of fish (*B. xanthopterus*) that collected during the study period

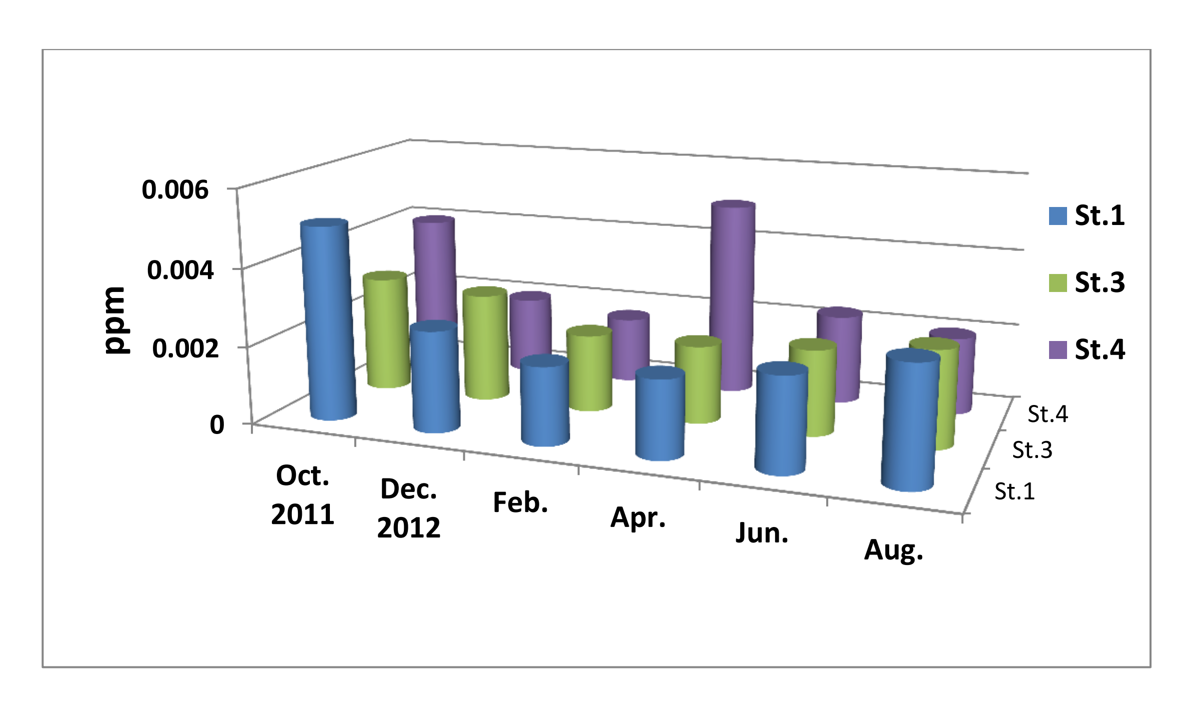


Figure (14): Variation of zinc in gills of fish (*B. xanthopterus*) that collected during the study period

3.1.3.3 Manganese (Mn)

In present study the concentrations of manganese were shown in Fig. 15, 16 and 17; Table 10, 11 and 12.

The maximum concentration (1 ppm) of manganese was recorded in gills of fish collected from station 1 in October 2011, while the minimum concentration 0.0024 ppm was found in muscle of fish collected from station 3 in June 2012.

The highest annual average of Mn concentration 0.089 ppm was observed in gills and the lowest was found in intestine and muscles (0.03 ppm).

Seasonally, the high concentrations were found in autumn, winter, and spring and the low in summer. Locational, the maximum concentrations were found in fish that collected from station 1, while the lowest in fish that collected from station 3 and 4. The statistical analysis of the data showed significant differences was found between fish that collected from stations for each muscle and intestine, while no significant differences observed between

fish collected from station 3 and station 4 for gills ($P<0.05$) (Table 10, 11 and 12).

In this study the concentrations of cadmium were lower than of other studied metals concentrations for water, sediments and fish. The results of this study showed that the gills contained the highest concentration of all detected heavy metals, followed by the intestine, while the muscle tissues appeared to be the least preferred site for the bioaccumulation of metals as the lowest metal concentration were detected in this tissue.

The maximum values and mean values of manganese within permissible limit in IAEA-407 (2005) cited in Wyse *et al.* (2005) and FEPA (1991) shown in Table 13.

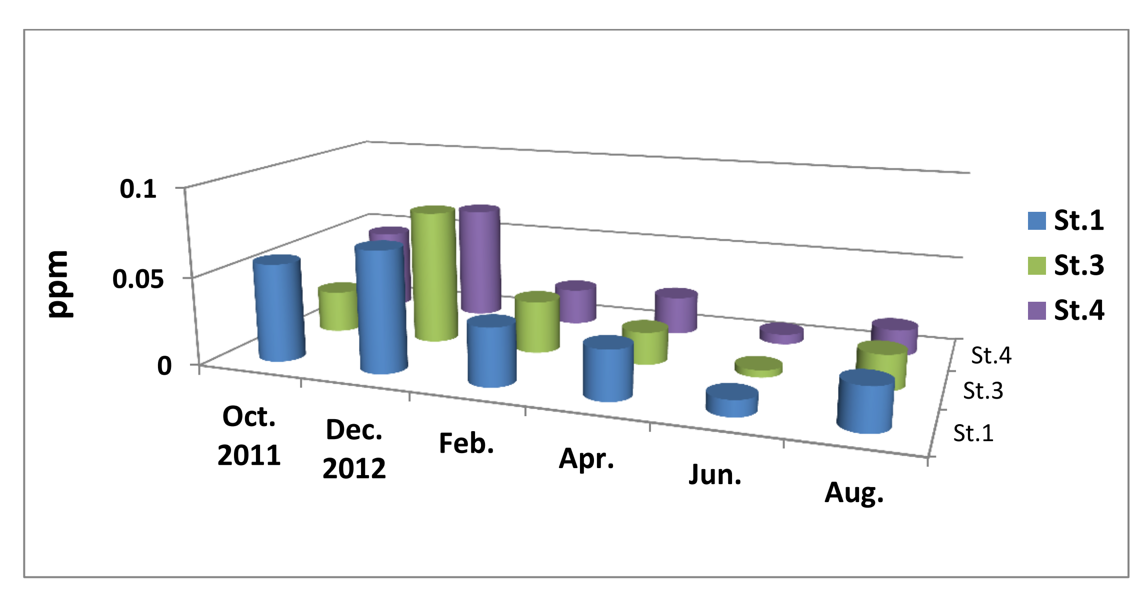


Figure (15): Variation of manganese in muscles of fish (*B. xanthopterus*) that collected during the study period

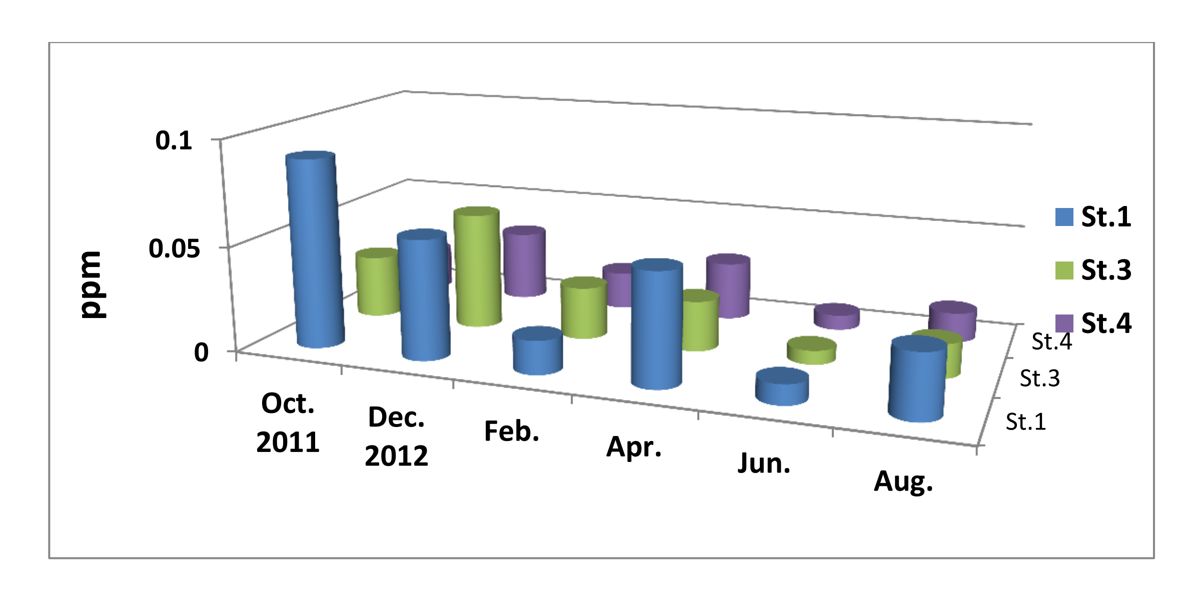


Figure (16): Variation of manganese in intestine of fish (*B. xanthopterus*) that collected during the study period

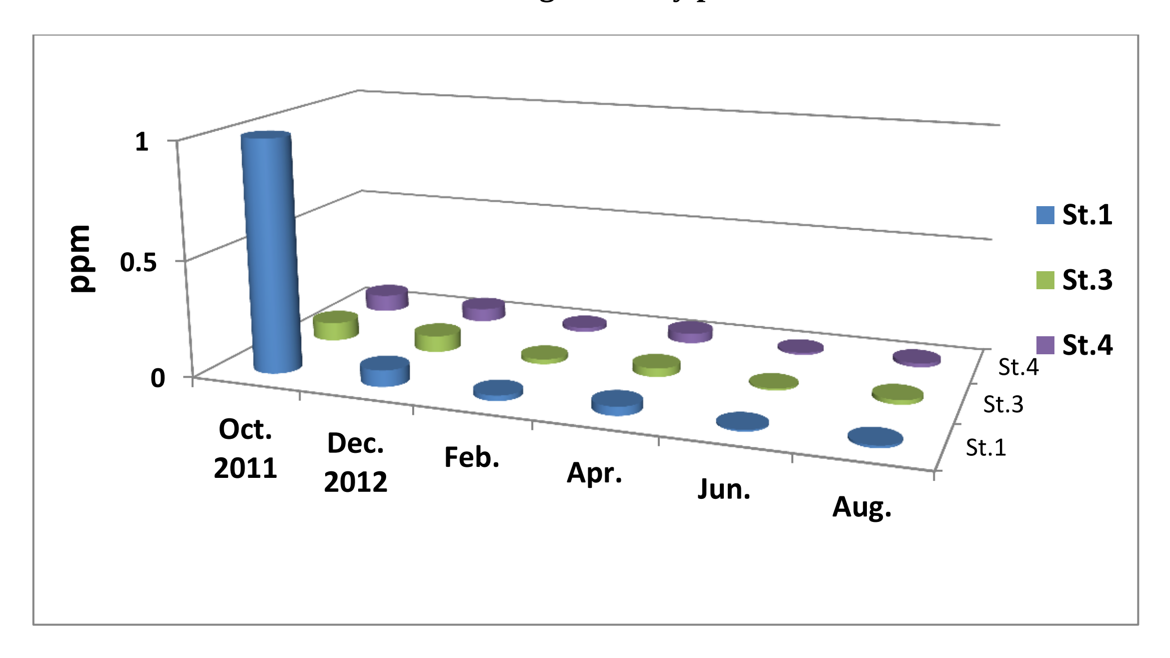


Figure (17): Variation of manganese in gills of fish (*B. xanthopterus*) that collected during the study period

The results of this study, the highest metal concentrations (except for Mn) was found in hot and warm seasons were because chemicals become more soluble in high temperature, the metabolic rate of aquatic organisms increase, growth rate will also increases with the decomposition of organic matter (Eggleton and Thomas, 2004).

However, it was evident from this study that, in general the gills was the site of maximum accumulation for the elements, while the muscle was the

overall site of least metal accumulation in this species. In fish, gills are considered to be the dominate site for contaminant uptake because of their anatomical and/or physiological properties that maximize absorption efficiency from water (Hayton and Baron, 1990). The high concentrations of metals in the gills could be due to the element complexion with the mucus that is virtually impossible to completely remove from the gill lamellae before prepared for analysis (Khail and Faragallah, 2008). Furthermore, the adsorption of metals onto the gills surface as the first target for pollutants in water could also be a significant influence in the total metal levels of the gill (Eneji *et al.,* 2011).

The increase in concentrations of metals in fish could be mainly due to metal contaminated diet, which comes from discharge of effluents in to rivers from different industries and other sources in the form of particulates and solution (Mount and Stephan, 1969). Accumulation of trace elements in aquatic organisms is one of the most striking effects of pollution in aquatic systems (Malhat, 2011). The mechanism of trace metals bioaccumulation in fish is complex and diversified, varying with their chemistry, mode of action and metals types (Louma, 1983). Heavy metals would become biologically magnified when taken up by the fish from the polluted waters and start accumulation in fish tissues- such uptakes are significantly pronounced in fish liver, gills, stomach, kidney, and other organs depending upon the exposed concentration and types of metals (Fabris *et al.*, 2006).

The accumulation of heavy metals in fish depends upon the concentration of the metals, exposure time, physiological condition of fish and environmental factors especially pH and hardness of water (Davies *et al.*, 1972; Donald, 1972).

Heavy metals in the aquatic environment can accumulate in fish tissues even at very low concentration therefore, the measurement can reflect the exposure effects. In general, active metabolite organs, such as gill, liver, and

kidney, often sensitively accumulate larger amount of metals that muscles. Different tissues have varied accumulating capacities of metals, which may be due to the different metabolic roles of metals and functions of organs (Ashraf, 2005). Moreover, heavy metal concentrations indifferent fish species might be a result of different ecological needs, metabolisms, and feeding pattern (Allen-Gill and Martynov, 1995).

These elements are known to produce adverse effects on aquatic biota and human health. Effects of these metals in fish include reduction of growth and reproductive capacity, swimming imbalance and inability to capture the prey (Patrick and Loutit, 1978).

Table (13): Compared study elements (Cd, Zn, and Mn) of fish (*B. xanthopterus*) that collected from Tigris River with the international standard limits

World Standards	Cd ppm	Zn ppm	Mn ppm
FAO (1983)	0.5	30	_
UNEP (1985)	0.30	_	_
FEPA (Federal Environment Protection Agency) (1991)	0.05	_	5.0
WHO (1993)	0.2	150	_
NSMD (National Standards Management Department) (2001)	0.1	_	_
IAEA-407 (International Atomic Energy Agency) (2005)	0.18	_	11.0
EC (European Commission) (2005)	0.05	_	_

Table (14): Compared studied elements (Cd, Zn, and Mn) of fish (*B. xanthopterus*) that collected from Tigris River with other local and international studies

Place	Metals / Fish types	Tissue types	Cd ppm	Zn ppm	Mn ppm	References
Arabian Gulf and the Shatt Al-Arab River, Iraq	*Mullet* *Nematolosa nasus*	Muscles	0.04 0.09	9.9 10.7	1.0 3.7	Abaychi and Al-Saadi (1988)
Ravi River, Pakistan	*Cyprinus carpio*	Muscles	0.51	1.65	0.2	Tariq *et al.* (1994)
Shatt Al-Arab	*Nematolosa nasus*, *Liza subviridi*	Muscles	0.03 0.03	7.34 8.58	1.33 1.79	Al-Khafaji (1996)
Al-Hilla River, Iraq	*B. sharpie*, *Asbius vorax*, *Cyprinus carpio*	Muscles	1.95 2.01 2.23	20.58 19.99 40.50	1.93 1.86 1.32	Al-Taee (1999)
Tigris River, Iraq	*B. grypus*	Muscles	ND-0.025	14.6-92.5	ND-1.72	Rasheed *et al.* (2001)
Tigris River, Iraq	*B. grypus*	Muscles	ND-2.95	6.5-20.5	_	Sabri *et al.* (2001)
Tigris River, Turkey	*Silirus triostegus*, *Mastacembelus simacks*	Muscles Gills Muscles Gills	ND ND ND ND	8.76 22.89 9.3 13.21	0.31 10.00 1.67 2.77	Karadede-Akinand and Ünlü (2007)
Ganges River, India	*Channa punctatus*, *Aorichthys aor*	Muscles Muscle	0.008 0.037	2.162 14.00	_ _	Gupta *et al.* (2009)

Okumeshi River, Nigeria	*Tilapia nilotica,* *Chrysichthys nigrodidatatus*	Muscles Gills Muscles Gills	0.62 0.21 1.89 0.14	_ _	1.97 0.17 0.45 0.13	Ekeanyanwu *et al.* (2010)
Yellow River, China	*Triplohysa pappenheimi,* *Gobio hwanghensis*	Muscles Gills Muscles Gills	0.024 0.024 0.03 0.028	4.327 4.645 5.668 32.097	_ _	Wang *et al.* (2010)
Ganga River, India	*Channa marulius,* *Aorichthys seengala*	Muscles Muscles	0.036 0.04	12.76 12.4	_ _	Aktar *et al.* (2011)
Tigris River, Iraq	*Cyprinus carpio*	Muscles Gills intestine	0.014 0.012 0.011	_	_	Al-Hammam (2012)
Tigris River, Iraq	*B. xanthopterus*	Muscles Gills Intestine	0.0043 0.012 0.0096	0.0023 0.0027 0.0023	0.03 0.089 0.03	Present study

3.2 Environmental parameters in Tigris River

3.2.1 Physical and chemical proprieties

3.2.1.1 Air and water temperature

Temperature is one of the most important among the external factors which influence aquatic ecology (Huet, 1986).

Air temperature affects on comprehensive process, which develops the life of organisms in the natural waters. Especially, it is influence on the dissolution of oxygen and other gases in water, value of pH and the salts dissolubility in water.

Temperature of water may not be as important because of the wide range of temperature tolerance in aquatic life of unpolluted water, but in polluted

water, temperature have profound effects on dissolved oxygen (DO) and biological oxygen demand (BOD) (Hacioglu and Dulger, 2009). Therefore, the temperature plays an important role in water by affecting on the rates of chemical reactions and the metabolic rates of organisms, as well as controlling the distribution of aquatic organisms (Anon, 1996). The fluctuation in river water temperature usually, depends on the season, geographic location, sampling time and temperature of effluents entering the stream (Ahipathi and Puttaiah, 2006).

The air temperature values in this study were varied from the lowest value 12^0C which was recorded at station 1 in December 2012 and the highest value 42^0C was observed in August 2012 at station 3. While the water temperature values were varied from lowest value 9^0C at station 1, 2 and 3 in December 2012 and the highest value was 32^0C at station 3 in August 2012. The annual average of air and water temperature was 28^0C and 20.6^0C, respectively (Fig. 18 and 19; Table 15).

Seasonally, the low values of air and water temperature were recorded during winter months and the high values were recorded during the summer months. The results of statistical analysis showed that there was a significant differences in air and water temperature among months except between Aug. 2012 and Jun. 2012 for water temperature, while no significant differences among stations ($P<0.05$) except between station 1 and station 3 for air temperature, that may be due to difference in time of samples collecting (Table 15). Increase of solar radiation due to comparatively longer day length may explain gradual increase in both air and water temperature from April to August. Similarly, a gradual reduction in solar radiation may explain fall in temperature from October to February and again it begins to increase from April onwards.

The recorded values for air and water temperature in the present study showed clear changes depending on the weather conditions during the period

of measure, the simple changes attributed to several environmental factors such as current water, depth of the water, benthic materials, temperature of effluents entering the water stream exposure to direct sunlight and the degree of shade (Bartram and Balance, 1996). The direct correlation between air and water temperature ($r = 0.975$) was observed in present study ($P<0.05$) (Table 16).

The directly correlation was observed between temperature and concentrations of studied heavy metals, but this correlation was not significant, depending on the values of the correlation coefficient recorded in this study (Table 17).

Oxygen is one of the most important gases Influenced by the heat of water body. It is less melting at high temperature and this is evidenced by statistical analysis that there was strong inverse correlation between DO and each of air and water temperature ($P<0.05$) ($r = -0.675$ for air temp. and $r = -0.621$for water temp.) (Table 16). The amount of dissolved oxygen in water is less as result of consumption of dead organisms by bacteria after rapid growth that caused by a speed of photosynthesis process as a result of the high temperature in the water body. Increased water temperature can also cause an increase in the photosynthetic rate of aquatic plants and algae and this can lead to increase plant growth and algae blooms. This phenomenon can be harmful effect on the ambient (Rundle *et al.*, 1993; Ormerod *et al.*, 1994).

The results of air and water temperature in this study were agreed with results of Al-Tameemi (2004) regarding to the variation of temperature of air and water were 9.7-37^{0}C and 9-30.6^{0}C, respectively. Nashaat (2010) found the temperatures of air and water were 9-41.5^{0}C and 9.8-34^{0}C, respectively. Wahab (2010) and Hashim (2010) who found in their studies the air and water temperature values were ranged between 15-40^{0}C and 11-30 ^{0}C, respectively. Abed Al-Razzaq (2011) found the values varied between 14-39^{0}C for air and 11-30^{0}C for water, Ahmed (2012) and Mustafa (2012) reported the air and

water temperatures were ranged 11-40^{0}C and 9-32^{0}C, respectively in Tigris River. The maximum limit of water temperature in this study exceeds the permissible limit, while the mean value of water temperature was found within the permissible limit of WHO standards (2004), which was between 25-30^{0}C.

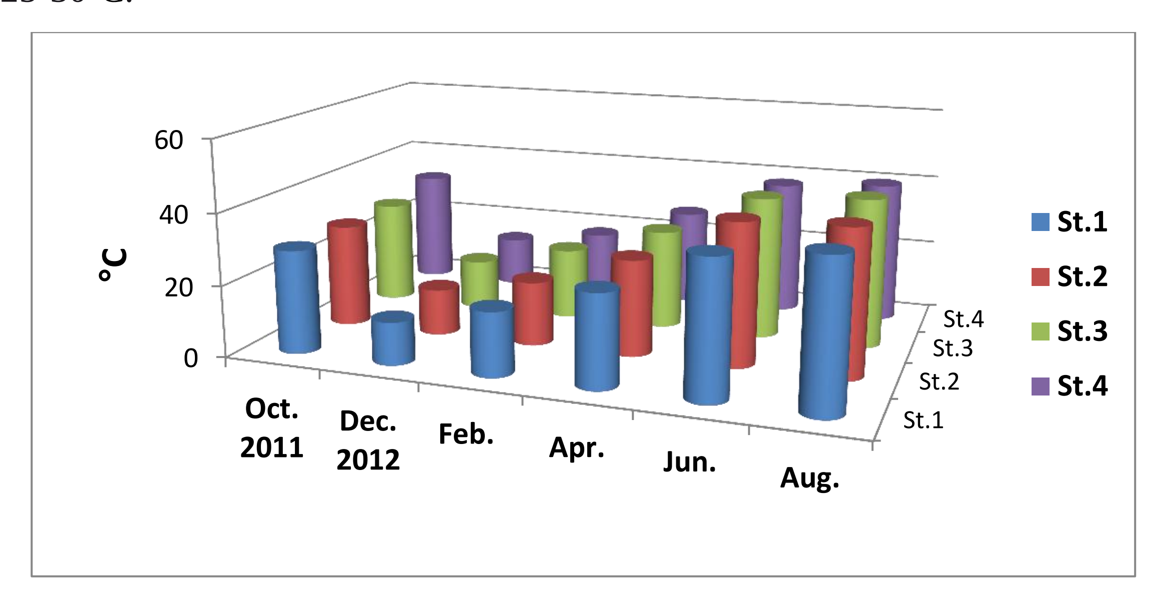


Figure (18): Variation of air temperature during the study period

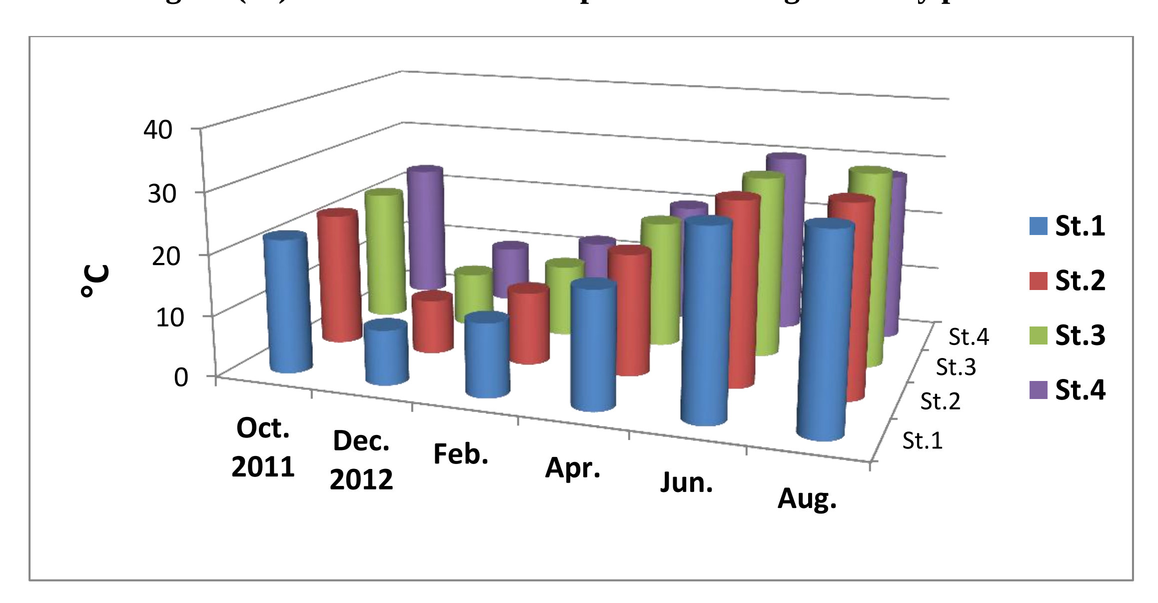


Figure (19): Variation of water temperature values during the study period

Table (15): The concentrations (Mean±SD) of different studied physical and chemical parameters in the river water of the four studied stations

Parameters		S1	S2	S3	S4
Air Temp. °C	Min	12	13	14	14
	Max	41	41	42	40
	Mean ± SD	27.33 ±10.6176 **a**	28 ±10.6605 **ab**	28.83 ±10.3312 **b**	28 ±10.0117 **ab**
Water Temp. °C	Min	9	9	9	9.5
	Max	31	31	32	30
	Mean ±SD	20.5 ±8.6381 **a**	20.66 ±8.6023 **a**	21 ±8.7514 **a**	20.41 ±7.9228 **a**
pH	Min	6.9	6.9	7	7.4
	Max	8	8	8.1	8.2
	Mean ±SD	7.56 ±0.5346 **a**	7.6 ±0.5357 **a**	7.61 ±0.5215 **a**	7.83 ±0.5346 **a**
EC µs/cm	Min	420	400	420	450
	Max	750	810	800	810
	Mean ±SD	526.66 ±120.6843 **c**	561.66 ±140.6393 **b**	556.66 ±135.1252 **b**	583.33 ±125.1352 **a**
TDS mg/l	Min	230	220	240	260
	Max	420	450	450	450
	Mean ±SD	296.66 ±68.5565 **c**	310 ±79.6499 **b**	315 ±75.0294 **b**	326.66 ±71.2080 **a**
DO mg/l	Min	5.92	5.88	5.65	6.11
	Max	8.33	10.47	10.97	10.5
	Mean ±SD	7.23 ±1.1073 **b**	7.46 ±1.8162 **ab**	7.53 ±1.9032 **ab**	8.0 ±1.7999 **a**
TSS mg/l	Min	474	490	450	518
	Max	824	810	860	844
	Mean ±SD	618.33 ±149.3602 **b**	611.66 ±131.3092 **b**	627 ±158.8369 **b**	655.55 ±143.7789 **a**
TH mg/l	Min	217.5	225	225	200

	Max	530	500	550	425
	Mean ±SD	340.41 ±110.5875 **b**	342.5 ±101.4925 **b**	368.33 ±110.2004 **a**	325.91 ±90.82 **c**

Different letters in same row that indicate for differences significance

Table (16): The correlation coefficient among studied water parameters

	Air Temp.	**Water Temp.**	**pH**	**EC**	**TDS**	**DO**	**TSS**
Water Temp.	0.975*						
pH	0.221	0.181					
EC	-0.421*	-0.416*	-0.349				
TDS	-0.418*	-0.411*	-0.348	0.987*			
DO	-0.675*	-0.621*	-0.283	0.585*	0.626*		
TSS	-0.227	-0.248	-0.317	0.846*	0.856*	0.515*	
TH	-0.427*	-0.434*	-0.416*	0.721*	0.741*	0.550*	0.789*

* Significant at ($P<0.05$)

3.2.1.2 Hydrogen ion concentration (pH)

The pH expresses the intensity of acidity or alkalinity of an aqueous solution. The pH of an aqueous system can be understood as estimation of the activity, or effective concentration, of hydrogen ions (H^+) affecting that system (Hem, 1989; Pankow, 1991). pH mathematical notation defined as the negative base ten logarithm of the hydrogen ion activity. Consideration of hydrogen ion concentration is important in almost all uses of water. In

particular, pH balance is important in maintaining desirable aquatic ecological conditions in natural waters.

The pH of aquatic ecosystem depends on chemical and biological activity in water. Natural water usually has pH highest than 7 (Durmishi *et al.*, 2008). It is important because many biological activities can occur only within a narrow range. Thus, any variation beyond acceptable range could be fetal to a particular organism (Iqbal *et al.*, 2004).

The pH range for diverse fish production is (6.5-9), while pH=4 considered acid death point, (4.0-5.0) no reproduction, (4.0-6.5) slow growth and 11.0 alkaline death point (Boyd and Tucker, 1998; Ali *et al.*, 2000).

The pH values of all stations are shown in (Fig. 20; Table 15). It was observed that range of pH was from 6.9 to 8.2. The minimum pH value 6.9 has been noted at station 1 and 2 in December 2012. The maximum pH value 8.2 was recorded at station 4 in October 2011. The annual average was 7.65. Seasonally, the low values of pH were recorded during the winter months while the high values were during the autumn months. The statistical analysis of the data showed no significant differences among stations at ($P<0.05$) (Table 15).

The variation in pH is due to the presence or absence of free carbon dioxide and carbonate, and planktonic density during various months. It is well documented the direct relationship between pH and CO_3 and the inverse relationship between pH and free carbon-dioxide (Zafar, 1964; Swarup and Singh, 1979; Jhingran, 1982).

In this study the narrow range of pH values in stations is attributed to high regulation capacity in hardness and alkaline water that rich in bicarbonate (Hynes, 1972; Goldman and Horne, 1983). As proven by statistical analysis results of this study the inverse correlation between pH and total hardness was observed ($r = -0.416$) ($P<0.05$) (Table 16). Iraqi waters

have alkaline nature that due to of the presence of calcium bicarbonate (Hassan, 2004; Salman, 2006).

Generally, the values of pH increases when the discharge is low, and also when the density of phytoplankton is high that lead to activation of photosynthesis process and high consumption of gas CO_2 that results the high value of pH in water (Goldman and Horne, 1983; Sabri *et al.*, 1989). The pH was relatively low in winter, while it was high during dry season. When the water level and the flow rate very low therefore, positive relationship between pH and each of air and water temperature was found in current study and this showed through statistical analysis ($r = 0.221$ for air temp. and $r = 0.181$ for water temp.) ($P<0.05$) (Table 16).

The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb the oxidation state of the mineral components and the redox environment of the system (Akcay *et al.*, 2003). The metals are generally precipitated at alkaline pH in the form of insoluble oxides and carbonates (Gupta *et al.*, 2009). In Table 17 the statistical analysis of pH showed weak positive correlation with dissolved heavy metals concentrations ($r = 0.119$ for Cd), ($r = 0.134$ for Zn) and ($r = 0.165$ for Mn) and this proves that pH value does not influence the dissolving of heavy metals that due to relative stability of pH values. It has been proved that lethality increases as oxygen concentration decreases. Zinc is generally considered a toxic element and its solubility is heavily depending on pH value; it is nearly soluble under neutral pH, but becomes much more soluble when pH drops to 6 (Förstner and Wittman, 1983; Alloway, 1990).

The present results agreed with Al-Tameemi (2004) who found that pH values were between 7.5-8.4 in Tigris River, Nashaat (2010) recorded that pH values were between 7.4-8.8 in Tigris River, Al-Janbi (2011) found the values of pH were between 7.1-8.4 in Tigris River, Ahmed (2012) and Mustafa

(2012) who found the pH values varied between 7.1-8.2 in Tigris River, and Al-Helaly (2010) reported that pH values were ranged between 6.9-8.2 in Al-Gharraf River. Whereas, these results disagree with other studies such as: Al-Nimrawee (2005) who found the pH value ranged between 6.7- 8.4, Wahab (2010) and Hashim (2010), they recorded the pH values were between 6.3-7.6 and Abed Al-Razzaq (2011) who found that pH values were ranged between 6.4-8.2 in Tigris River. In this study the maximum value and the mean value of pH was within permissible limits of Iraqi standards of river water 1967 No. (25) and WHO standards (2004), which were between 6.5-8.5.

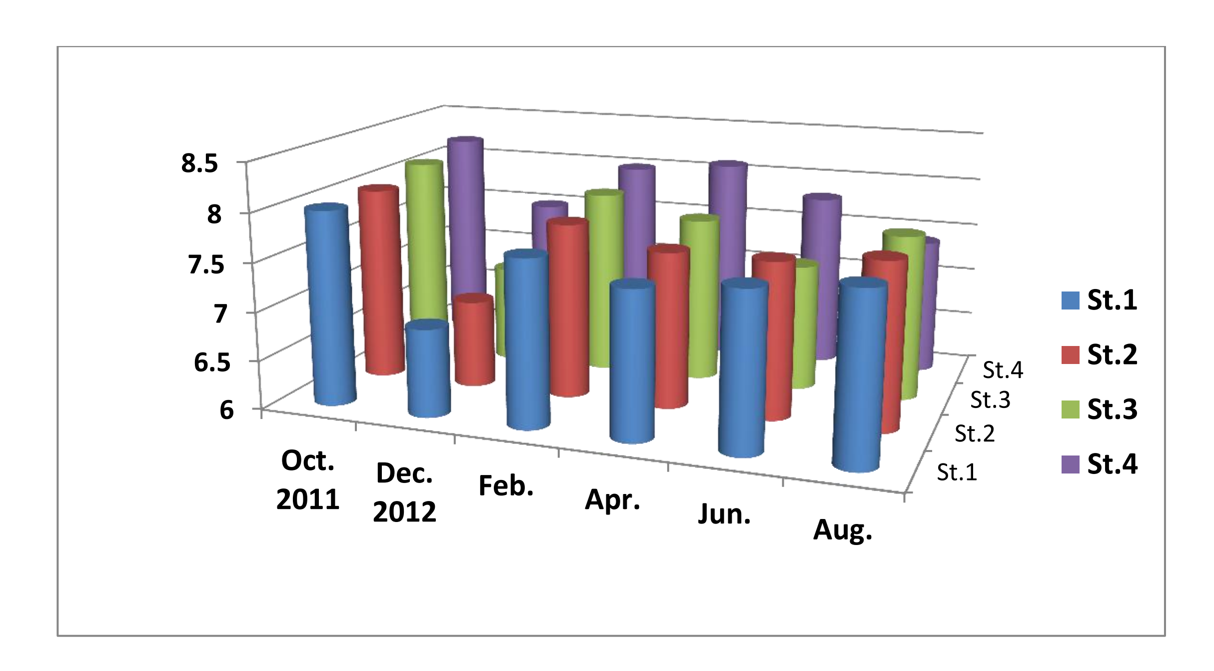


Figure (20): Variation of pH values in Tigris River during the study period

Table (17): The correlation between studied dissolved heavy metals and water parameters

	Air Temp.	Water Temp.	pH	EC	TDS	DO	TSS	TH
Cd	0.308	0.311	0.119	-0.274	-0.227	0.022	0.059	0.043
Zn	0.225	0.220	0.134	-0.551 *	-0.523 *	-0.033	-0.295	-0.387
Mn	0.091	0.046	0.165	-0.017	0.027	0.144	0.352	0.335

* Significant ($p<0.05$)

3.2.1.3 Electrical conductivity (EC)

Electrical Conductivity defines as ability of 1 cm^3 of water to conduct an electrical current at temperature 25^0C. The types of salts (ions) causing the conductivity usually are chlorides, sulphates, carbonates, sodium, magnesium, calcium, and potassium (WASC, 2002). Natural water possesses low conductivity but will increase when the pollution occurs.

The range of electrical conductivity of this study was 400 to 810 µs/cm (Fig. 21; Table 15). The lowest conductivity value (400 µs/cm) was recorded at station 2 in April 2012 and the highest value (810 µs/cm) was recorded at station 2 and 4 in December 2012. The annual average of electrical conductivity was 557 µs/cm. The statistical analysis revealed significant differences ($P<0.05$) in EC among months and the significant differences ($P<0.05$) found among stations except between station 2 and station 3 (Table 15).

Seasonally, the low values were observed during the spring months; whereas, the high values were found in winter months. In this study the high EC values were recorded during the winter months may be because the high concentrations of total dissolved substances in the water, which come from rains and the soil drift (Welcomme, 1979). This explanation confirms the

results of current study, as we found the strong positive correlation between EC and total dissolved solids (TDS) ($r = 0.987$) ($P<0.05$) (Table 16). The lowest EC values were found during spring and summer months may be related with melting of snow, speed of river flow and the difference in the quality of the rocks these lead to dilute the water and then drop the values of EC (Welcomme, 1979).

The high value of EC is companied with high concentration of dissolved salts, and depending on type of present ions and their concentrations, and may be due to what the river carrying of tons of sandy sediments and different elements that contain the salts (Detay, 1997). This agrees with statistical analysis results that showed strong positive correlation between EC and each of total suspended solid (TSS) and total hardness (TH) ($r = 0.846$ for TSS and $r = 0.721$ for TH) ($P<0.05$) (Table 16). In Table 17 the statistical analysis results of EC showed inverse correlation between EC and dissolved heavy metals concentrations ($r = -0.274$ for Cd), ($r = -0.551$ for Zn) and ($r = -0.017$ for Mn).

The results of present study conflicted on the study of Al-Tameemi (2004), Wahab (2010), Hashim (2010), Ahmed (2012) and Mustafa (2012) on Tigris River, and Al-Helaly (2010) on the Al-Gharraf River, Salman (2006) on the Euphrates River. While, the low result of this study agree with low result that recorded by Nashaat (2010) and Abed-Al-Razzaq (2011) on Tigris River. In present study, the maximum value of EC is above the favorable limit while, the mean value was recorded within the permissible limit of 750 µs/cm in water (WHO, 2004).

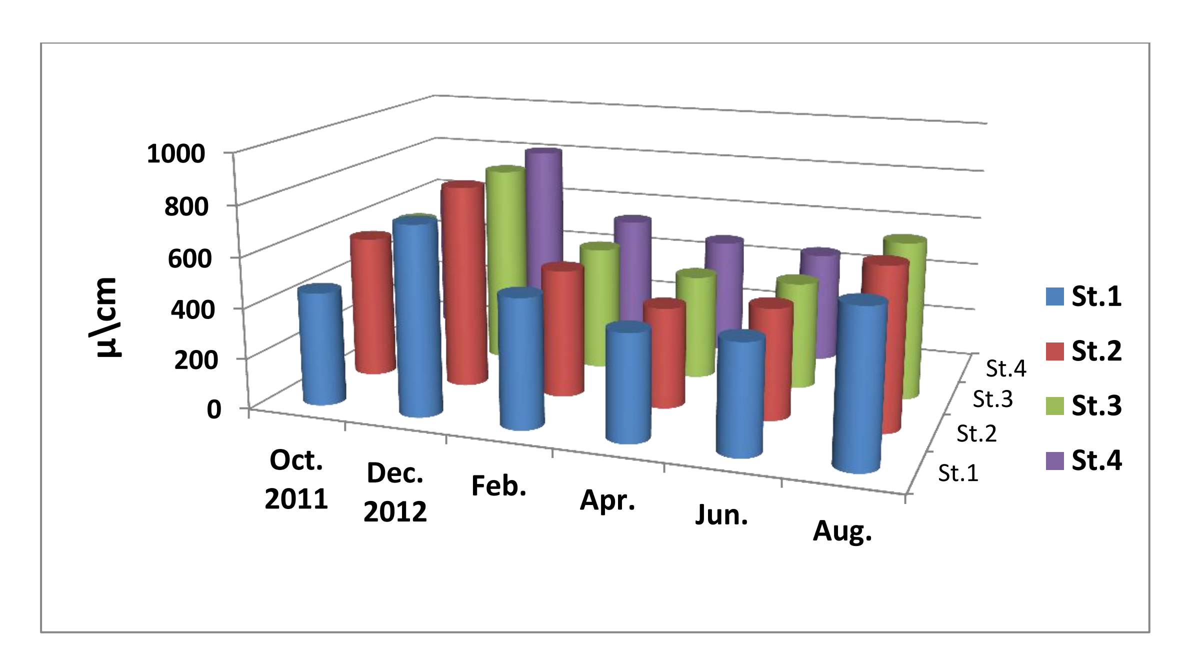


Figure (21): Variation of electrical conductivity during the study period

3.2.1.4 Total dissolved solids (TDS)

TDS is used as a general indicator of water quality; TDS is a measurement of minerals, in organic salts and organic matter in water. TDS is that portion of solids in water that can pass through 0.45µm (McCulloch *et al.*, 1993; Zipper and Berenzweig, 2007). The amount of total dissolved solid depends on water sources, and water that pass through soils have high soluble salts or minerals that have higher TDS levels. High TDS occur when water receives agricultural or urban runoff (Park *et al.*, 2002). TDS content showed fluctuations according to seasonal basis (Fig. 22; Table 15).

The maximum TDS value (450 mg/l) was found at station 2, 3 and 4 in December 2012, while the minimum value (220 mg/l) was found at station 2 in April 2012. The annual average of TDS was 311.6 mg/l. The statistical analysis showed a significant differences ($P<0.05$) among months except between October 2011and February 2012 and between April 2012 and June 2012 and significant differences ($P<0.05$) was found among stations except between station 2 and station 3 (Table 15).

Seasonally, the high values of TDS were noted during winter months; whereas, the low values were recorded during the spring months. This agrees

with statistical analysis results that showed the inverse correlation between TDS and each of air and water temperature (r = -0.418 for air temp. and r = -0.411 for water temp.) ($P<0.05$) (Table 16). The high value of TDS was seen in winter months due to winter is rainy season in study area so, when descending rains especially in crowded cities and industrial areas, which attributed with high pollution in the atmosphere. The pollutants dissolve in water of rain and arrive to rivers, which lead to increase the TDS in water (Prasad and Freitas, 2000).

Langmuir (1997) explained the values of TDS increase with increasing the quantity of water in the waterway that due to contact the water with rocks and this agrees with statistical analysis results of current study that found the strong positive correlation with total hardness (r = 0.741) ($P<0.05$) (Table 16), while Boyd (2000) focused on the effect of human factor on the increase of TDS value through the discharge of large amounts of sewage from cities.

The low values were found during spring, autumn, and early stage of summer (June month), that may be due to affect of dilution factor (Al-Mussawi *et al.*, 1995). Whereas, the values of TDS increase in August month because the high temperature evaporates the river water therefore, the TDS value will be high. The results of statistical analysis for TDS showed inverse correlation with each of Cd and Zn, and that pointed to melt of these heavy metals in inverse relationship with TDS, but weak positive correlation was found with concentration of Mn (r= -0.227 for Cd, r = -0.523 for Zn and r = 0.027 for Mn) (Table 17). The study results disagree with other results of Wahab (2010), Hashim (2010), and Nashaat (2010) on Tigris River and, Al-Helaly (2010) on Al-Gharraf River, and Salman (2006) on Euphrates River, whereas the low result of this study agrees with the low result that found by Al-Tameemi (2004), Abd Al-Razzaq (2011), Ahmed (2012), and Mustafa (2012) on Tigris River. It was found that the maximum value and the mean

value of TDS within permissible limit set by WHO standards (2004) the limit was 1500 mg/l.

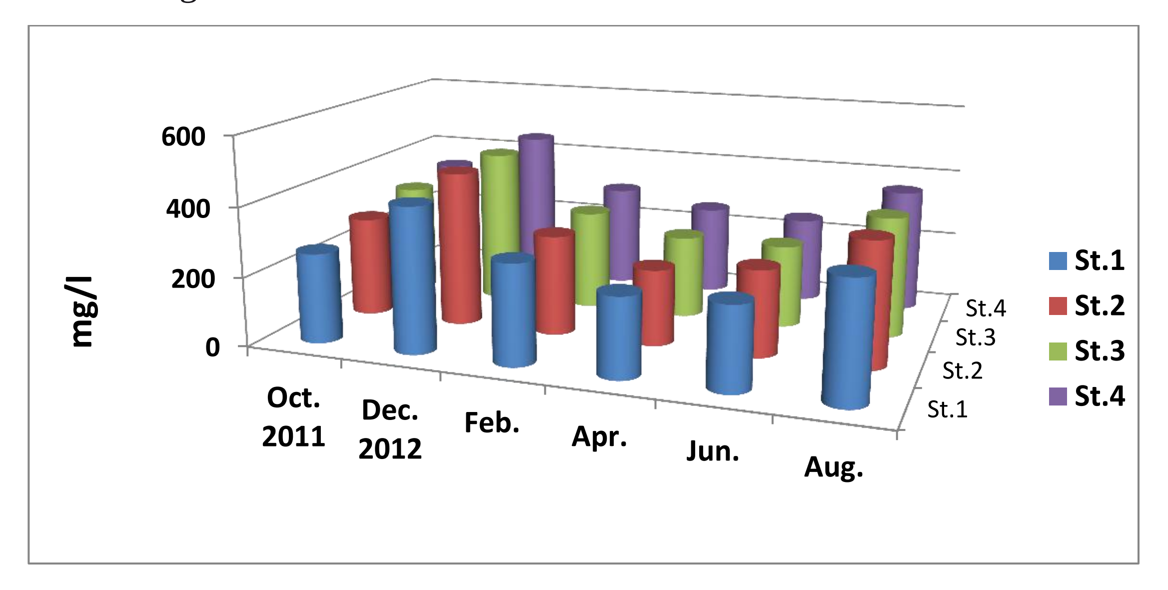


Figure (22): Variation of total dissolved solids during the study period

3.2.1.5 Dissolved oxygen (DO)

Dissolved oxygen refers to the oxygen gas that is dissolved in the water and made available to aquatic life. Oxygen enters the water through photosynthesis in aquatic plants or from the transfer of oxygen between the air and water (waves, turbulence, currents, etc). The oxygen diffuses in water very slowly. The quantity of dissolved salts and temperature greatly affects on the ability of water to hold oxygen. The solubility of oxygen increases with decrease the temperature (Singh *et al.*, 1990).

Fast-moving water, low temperature and low salinity result in the more dissolved oxygen. Dissolved oxygen combined with other important elements such as carbon, sulphur, nitrogen and phosphorous that could have been toxicants in the absence of oxygen in the water bodies to form carbonate, sulphate, nitrate and phosphate respectively that constitute the required compounds for aquatic organisms for survival (Biswas, 1973).

Dissolved oxygen is the most important parameter for protecting fish since most fish cannot survive when DO content is less than 3 mg/l (Chang, 2005). Fish growth is not only affected by rates of feeding and quality of the

food but is also affected by environmental changes that taking place, as metabolism rates of fish will increase by availability of food has dramatically, but the process of absorption will affect by lower concentration of dissolved oxygen that requirement necessary for fish (Viggor and Hellat, 2003).

There are many factors play an important role with fluctuations of dissolved oxygen concentration in water, in addition to photosynthesis and aquatic organism's respiration (Mermillod-Blondin *et al.*, 2003; Al-Kinzawi, 2007); the temperature will control on amount of dissolved oxygen.

The minimum concentration of dissolved oxygen was 5.6 mg/l recorded at station 3 in June 2012, while the maximum value (10.9 mg/l) was recorded at station 3 in December 2012. The values of DO at different stations during this study have been shown in Fig. 23; Table 15. The annual average of dissolved oxygen was 7.5 mg/l.

Seasonally, the low values of dissolved oxygen were recorded during the summer months, while the high values were found during winter months. The statistical analysis of the data showed no significant differences ($P<0.05$) among stations except between station 1 and station 4 (Table 15).

The pattern of dissolved oxygen is closely related with the changes of water temperature and this relation is an inverse relationship. The relationship between dissolved oxygen and free carbon dioxide is an inverse relationship well known (Horne and Goldman, 1994). This agrees with results of statistical analysis of present study that showed a negative correlation between DO and pH ($r =-0.283$) ($P<0.05$) (Table 16).

As was expected the highest value of DO was recorded during winter months may be due to temperature in this season was low (Macan, 1980). The lowest value was observed during summer months that may be due to no rainfall and increase in temperature in these months that lead to decrease in dissolved oxygen results to activate the photosynthesis due to the rate of oxygen consumption from aquatic organisms and high rate of decomposition

of organic matter in high temperatures of water (Abawei and Hassan, 1990; Al-Saadi, 2006a, b). Low concentration of dissolved oxygen may due to increase organismal respiratory demand at high temperature (Rao, 1986). Increase in temperature also increases toxicity due to depletion in dissolved oxygen, increase in energy demand causing rise in respiration rate in the organism, which leads to rapid assimilation of wastes (Bonga and Lock, 2003). The results of statistical analysis between dissolved heavy metals concentrations and DO showed very weak positive correlation for Cd and Mn but very weak negative for Zn (Table 17).

The results of present study agreed with the studies of Al-Tameemi (2004) who found that DO values between 6.5-9.8 mg/l in Tigris River, Nashaat (2010) who recorded in his study DO values was ranged between 5.9-9.5 mg/l in Tigris River and Al-Helaly (2010) recorded DO values varied between 6.0-10.1 mg/l in Al-Gharraf River. The low result of present study also agree with the low result that recorded by Hashim (2010) and Wahab (2010) they found that low DO value was 4.06 mg/l, also study of Ahmed (2012), and Mustafa (2012) observed that low value was 4.91 mg/l. The results of this study disagree with study of Abd Al-Razzaq (2011) in Tigris River; she recorded the values of DO between 1.82-8.7 mg/l and Al-Tameemi (2004) who found that values of Do were between 7.2-8.1 mg/l in Diyala River. The minimum concentration and the mean concentration of DO were within the permissible limit for both Iraqi standards river water 1967 No. (25), which was more than 5 mg/l, and within WHO standards (2004), which was 4 mg/l.

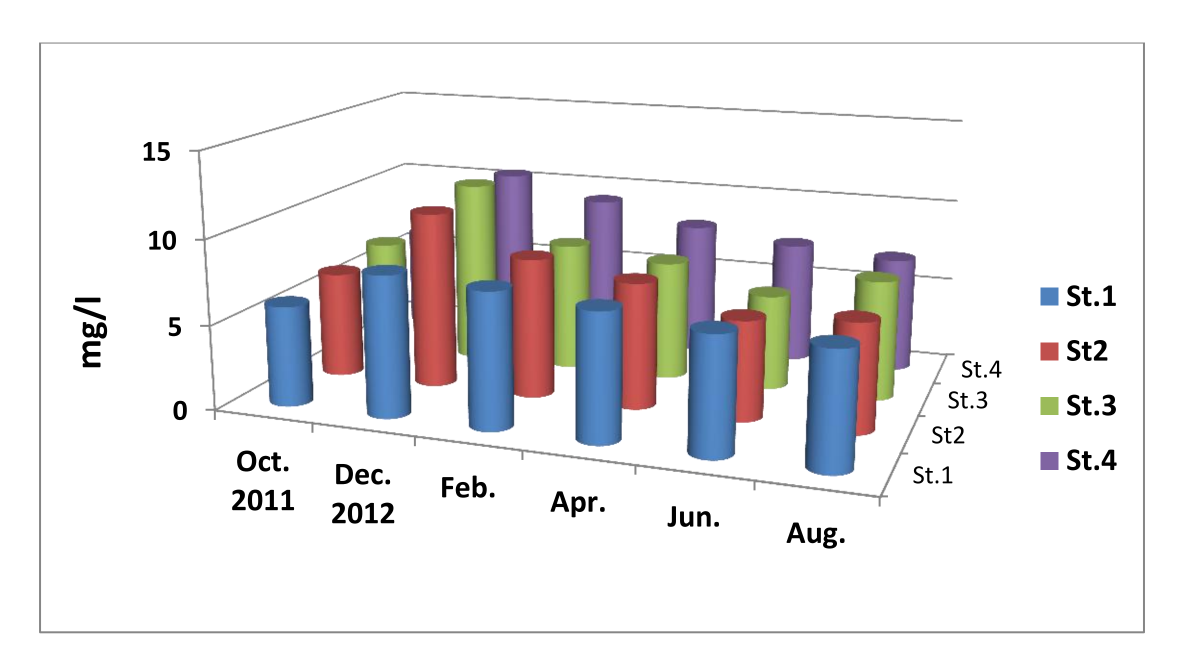


Figure (23): Variation of dissolved oxygen during the study period

3.2.1.6 Total suspended solids (TSS)

The term total suspended solids can be referred to materials which are not dissolved in water and are non-filterable in nature. It is defined as residue upon evaporation of non-filterable sample on a filter paper (APHA, 1998).

Total suspended solids varied between 450-844 mg/l in all study stations, the lowest value 450 mg/l was recorded at station 3 in June 2012 and highest value 844 mg/l was found at station 4 in December 2012. The annual average of TSS was 628 mg/l (Fig. 24; Table 15).

Seasonally, the low values of TSS were found during the summer months, whereas the high values were during winter months. The statistical analysis showed a significant differences ($P<0.05$) among months except between October 2011and April 2012 and between December 2012 and August 2012, but no any significant differences among stations was observed except with station 4 ($P<0.05$) (Table 15).

The results of present study showed clear increase in TSS values in winter months that may be due to rainfall that carried with it a lot of TSS such as dusts. While, the low values of TSS were found in autumn, spring, and early stage of summer (June month) in comparison with winter values. The

values of TSS in this study were ranged between (450-844) mg/l which was higher than the results of Al-Tameemi (2004) who found the values of TSS were varied between 4-24 mg/l, Al-Nimrawee (2005) who recorded the values of TSS were ranged between 10-235 mg/l, Wahab (2010) and Hashim (2010) who recorded the values of TSS were varied between 0.22-9.12 mg/l, and Ahmed (2012) who found that TSS values were varied between 28-350 mg/l in Tigris River, and Salman (2006) was found these values were ranged between 0.1-58.6 mg/l. The mean value of TSS in this study exceeds the permissible limit (50 mg/l) of WHO standards (2004).

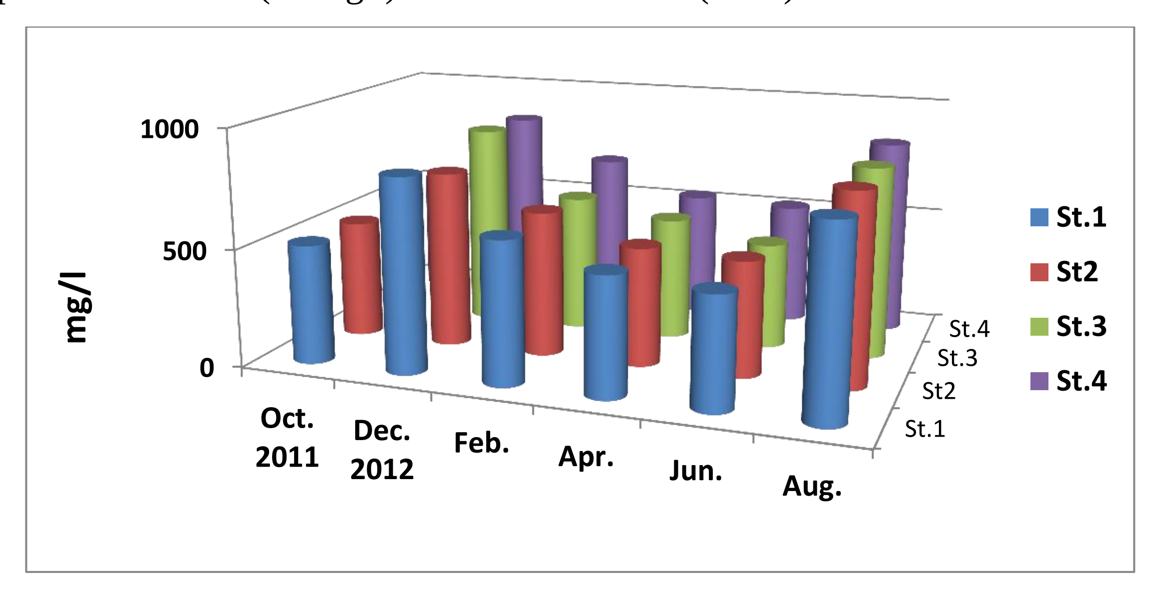


Figure (24): Variation of total suspend solids during the study period

3.2.1.7 Total hardness (TH)

Total hardness is numeric expression for the water content from metals, particularly, Ca^{+2}, Mg^{+2} and other alkaline metals, and is one of the main characteristics that vary according to quality of water around the world (Cech, 2003; WC, 2004). Water hardness is very important parameter for water quality and from this water use in many industrial branches. It depends from the presence of ions Mg^{+2}, Ca^{+2} and at the same time presents the sum of carbonate and non-carbonate hardness (Durmishi *et al.*, 2008).

The principal natural sources of hardness in water are dissolved polyvalent metallic ions from sedimentary rocks, seepage and runoff from soils, Calcium and Magnesium, are the principal ions which are present in many sedimentary rocks, most common being limestone, the other polyvalent ions, are aluminum, barium, iron, manganese, strontium and zinc (WHO, 2011). The values of total hardness in present study are shown in (Fig. 25; Table 15). The maximum value 550 mg/l of hardness was recorded at station 3 in December 2012, while the minimum value (200 mg/l) was found at station 4 in October 2011. The annual average value of TH was 342.9 mg/l. The statistical analysis revealed significant differences in TH among months except between February 2012 and August 2012, and significant differences ($P<0.05$) found among stations except between station 1 and station 2 (Table 15).

Seasonally, the high values were recorded during winter months and the low values were observed during the autumn and spring months. The increase of TH value in winter months in comparison with autumn month may be due to the rainfall on the ground and the discharge will increase from neighboring river lands (Halbeisen, 2003; Skipton *et al.*, 2004). According to Maulood and Hinton (1978); Al-Sangery (2001) the concentrations of hardness will increase with heavy rainfall in Iraq. The increase of hardness may be due to caulis nature of Iraqi soils, whereas decrease in spring months and again increase in summer months due to dust storms and precipitation of large amounts of dust that rich in minutes $CaCO_3$ and high concentrations of salts and this accords with what mentioned by Park *et al.*, (2002). USEPA (2000) classified waters according to $CaCO_3$ as the following: 50-150 mg/l is moderately hard water, 150-300 mg/l hard water, and more than 300 mg/l very hard water. According to this classification of water hardness the water of Tigris River was classifications to be very hard water.

The results of correlation coefficient for total hardness with studied heavy metals showed weak positive relationships with Cd and Mn, and weak inverse relationship with Zn (Table 17).

The study results agree with Al-Nimrawee (2005), who found that TH values were varied between (221-547) mg/l. These results also agree with previous studies of Al-Tameemi (2004) who recorded these were values ranged between 239-600 mg/l, Nashaat (2010) who recorded the TH values were ranged between 120-700 mg/l, Wahab (2010) and Hashim (2010) who found in their studies that TH values were varied between 255-492.5 mg/l, Ahmed (2012) and Mustafa (2012) who recorded the TH values were varied between 185-540 mg/l in Tigris River. While, Abd Al-Razzaq (2011) in Tigris River and Salman (2006) in Euphrates River found the values of TH ranged from 550 to 730 mg/l and 210 to 820 mg/l respectively, and these values considered higher than those values, which were reported in this study. In comparison with WHO standards (2004) the maximum level of TH was slightly favorable limit and the mean value of TH was found within permissible limit, which was 500 mg/l, whereas the permissible limit of Japanese guidelines was 300 mg/l.

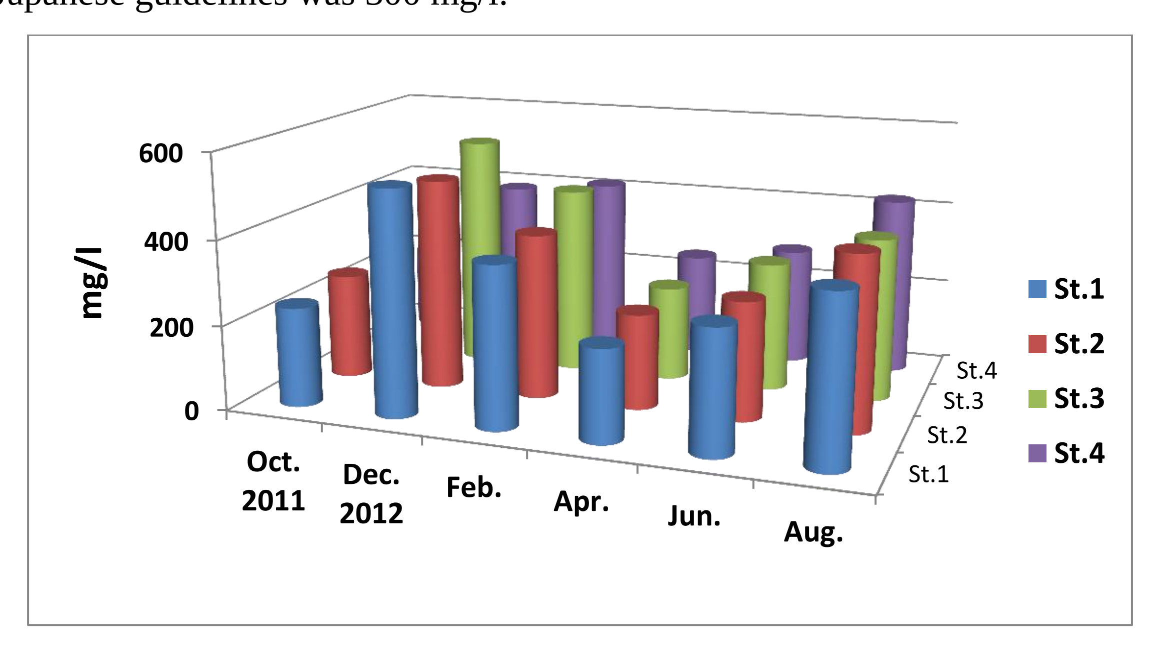


Figure (25): Variation of total hardness during the study period

3.2.2 Sediment texture

Texture refers to the size of the particles that make up the soil. The terms sand, silt, and clay refer to relative sizes of the soil particles. Sand, being the larger size of particles, feels gritty. Silt, being moderate in size, has a smooth or floury texture. Clay, being the smaller size of particles, feels sticky (Whiting *et al.*, 2011).

Soil texture is an important soil characteristic that drives crop production and field management. The textural class of a soil is determined by the percentage of sand, silt, and clay (Berry *et al.*, 2007).

Sediment texture at study stations showed that the station 1, 2, and 4 have sandy clay loam, while the station 3 was clay loam (Table 18).

As was expected the most widespread grain size in the sediments of Tigris River was the sand grains. The results of the present study showed that there was similarity for sediment texture of all the study stations were sandy clay loam except the third station was clay loam.

Table 18: Sediment texture in the studied stations of Tigris River during study period

Sediment type % (mm)	**S1**	**S2**	**S3**	**S4**
Clay (<0.002)	29.91	26.53	30.25	22.12
Silt (0.002 – 0.05)	22.73	21.19	25.41	19.34
Sand (0.05 – 0.10)	47.36	52.28	44.34	58.54
Evaluation	Sandy clay loam	Sandy clay loam	Clay loam	Sandy clay loam

3.2.3 Total organic carbon (TOC) in sediments

TOC measurement provides information on all organic substance content in sediments (Dojlido and Best, 1993). The determination of concentration of TOC in sediment and soil samples is an important parameter on environmental evaluation and investigation of the quality of the environment (Laze *et al.*, 2011).

Total organic carbon has a major influence on both the chemical and biological processes that take place in sediments. The amount of organic carbon has a direct role in determining the redox potential in sediment, thus regulating the behavior of other chemical kinds such as metals. Since organic matter is a primary source of food for benthic organisms, it is important in maintaining a viable ecosystem. However, too much organic matter can lead to the depletion of oxygen in the sediment and overlying water, which can have a deleterious effect on the benthic and fish communities (Wells, 2003). Total organic carbon (TOC) content in sediments has been used as an indicator of pollution and eutrophication rate (Folger, 1972; EPA, 2002).

The study results showed that there was similarity in all study stations whereas, the results showed the high values (0.57, 0.55)% were recorded at station 1 and 3 respectively, while the low values (0.45, 0.42)% were observed at station 2 and 4, respectively. These results agreed with study of Al- Taee (1999) on Al- Hilla River sediments as the concentrations ranged between 0.48 - 0.62%.

3.3 Ecological indices

3.3.1 Assessment of studied heavy metals pollution in Tigris River sediments

In recent years, a large number of studies on heavy metal pollution in sediments were performed, and many ways of assessing heavy metal pollution in sediments were proposed, such as geo-accumulation index, enrichment factor, pollution load index, and potential ecological index (Singh *et al.,* 2003; Burton *et al.,* 2005; Caeiro *et al.,* 2005; Visuthismajarn *et al.,* 2005; Chen *et al.,* 2007; Rodriguez-Barroso *et al.,* 2009).

3.3.1.1 Geo-accumulation index (I-geo)

I-geo index proposed by Müller (1969) and this I-geo method used to calculate the metal contamination level in river sediments. Karbassi *et al*. (2006) observed I-geo values can be used effectively and more meaningful in explaining the sediment quality. I-geo grades for the study area sediments vary from metal to metal and station to station.

According to, Geo-accumulation index all stations are unpolluted for Zn and Mn (average I-geo ≤ 0). Station 1 is slightly polluted (0 < average I-geo ≤ 1) with Cd, while the stations 2, 3 and 4 are moderately polluted with Cd (1< average I-geo ≤ 2). I-geo values of studied heavy metals in sediments are shown in Table 19.

This suggests that the sediments of Tigris River are having background concentrations for Zn and Mn and these elements are practically unchanged by anthropogenic influences, while the concentration of Cd exceeded the average shale value. The dangerous metal Cd may be derived from industrial waste and gasoline additives used, in the factories and cars (Mwamburi, 2003). This may be also derived through corrosion of the numerous abandoned launches along the river and agricultural activities.

Table (19): Geo-accumulation index (average I-geo values) for studied heavy metals in sediments of Tigris River

Stations	Average I-geo values		
	Cd	Zn	Mn
1	0.89	-0.60	-1.78
2	1.02	-0.64	-1.77
3	1.18	-0.47	-1.75
4	1.31	-0.32	-1.73

3.3.1.2 Pollution Load Index (PLI)

Pollution severity and it is variation along the sites was determined by using pollution load index (Adebowale *et al.* 2009). Tomlinson *et al.* (1980) explained that the application of PLI provided a simple way in assessing sediment polluted or not polluted. It is vital that all the necessary variables for the construction of PLI would be readily available. The station 1 and 2 can be classified as no pollution areas, where PLI values < 1, while station 3 and 4 had PLI values >1 confirming there were considerable contamination for studied heavy metals according to the classification of Harikumar *et al.* (2009). Variation of PLI of sampling stations was shown in Fig. 26; Table 20.

These results may be due to found many factories and hospitals and their discharges and sewage discharges flow to the river, and these releasing a lot of pollutants into the river without any real treatments.

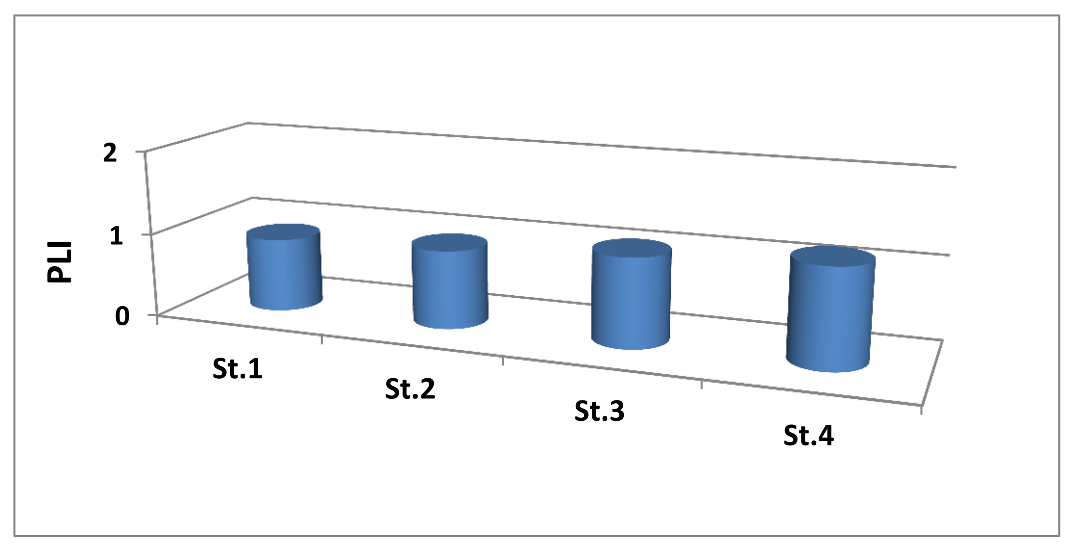


Figure (26): Variation of metal pollution index of heavy metals in sediments of Tigris River

3.3.1.3 Contamination Factor (C_f) and Degree of Contamination (C_d)

Maximum value of contamination factor was noticed for cadmium at station 4 was 5.6; while the minimum value of contamination factor (C_f) was recorded for manganese at station 1 and 2 (Table 20).

In present study, all stations recorded considerable contamination factor values for cadmium ($3 = C_f < 6$) according to the Hakanson's classification (1980). The station 1, 2 and 3 had low contamination factor values for zinc ($C_f < 1$), while the station 4 recorded a moderate contamination factor for this metal ($1 \leq C_f < 3$). Manganese exhibited low contamination factor for all investigated stations ($C_f < 1$).

The station 4 showed the maximum value of degree of contamination, while station 1 recorded the lowest degree of contamination (Table 20). The station 1 and 2 recorded low degree of contamination ($C_d < 6$), whereas the rest of stations were moderate degree of contamination ($6 = C_d < 12$).

From these indexes the study area was considered as a higher contamination with cadmium and zinc metals than Mn metal that due to influence of external discrete sources like industrial activities, agricultural

runoff and other anthropogenic inputs. Also use of chemical fertilizers and pesticides in the agricultural activities are considered additional sources of pollution (Salameh, 1996). Cadmium is relatively a rare metal. It has no essential biological function and it is highly toxic to plant and animals. The major hazard for human health by Cd is chronic accumulation of Cd in kidney (Alloway, 1990).

Table (20): Contamination factor (C_f), degree of contamination (C_d) and pollution load index (PLI) of sediment samples that collected from Tigris River

Stations	C_f values			C_d	PLI
	Cd	Zn	Mn		
1	3.36	0.81	0.25	4.42	0.88
2	4.2	0.78	0.25	5.23	0.93
3	4.93	0.93	0.26	6.12	1.06
4	5.6	1.08	0.26	6.94	1.16

3.3.1.4 Enrichment Factor (EF)

In present study, the enrichment factor (EF) is used to assess the level of contamination and the possible anthropogenic impact in the sediments of the river, to identify anomalous metal concentrations. According to Zhang and Liu (2002), EF values varied between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, where EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. A reference element is often a conservative one, such as the most commonly used elements Al, Fe, Mn, Se, Ti, etc. (Bergamaschi *et al.*, 2002; Mishra *et al.*, 2004; Yongming *et al.*, 2006).

In this study, manganese (Mn) was used as a reference element as it mainly originates from natural lithological sources.

Enrichment factors were calculated from the concentration of heavy metals in the study area (Table 21). The EF for Zn, remains in the range 2-5 in all stations indicates moderate enrichment. The high values of enrichment factor for Cd ranged between 5-20 refer to the station 1, 2 and 3 were significant enrichment by these metals, while station 4 was recorded very high enrichment (20-40). Therefore, the heavy metal pollution of study area was likely to originate from anthropogenic activities.

Table (21): Enrichment factor of heavy metals of sediment samples that collected from Tigris River

Stations	EF values	
	Cd	Zn
1	14.56	3.24
2	16.55	3.10
3	19.04	3.61
4	21.18	4.10

3.3.1.5 Potential Ecological Risk Index (E^i_f)

Investigation of heavy metal concentrations in surface sediments reveal to the degree of pollution over fresh water ecosystems. The effect and degree of the heavy metal pollution over river sediments were described by the Hakanson (1980) to assess ecological risks for aquatic pollution control.

According to potential ecological risk index for heavy metals, contamination of Cd reach to the high degree of potential ecological risk = (80-160) at station 1, 2 and 3, while the station 4 recorded very high degree of potential ecological risk index (> 160). The contamination of Zn showed the lowest degree of potential ecological risk index (< 20) at all studied stations (Table 22). The difference in indices results due to the difference in sensitivity of these indices towards the sediment pollutants (Praveena *et al.*,

2007). The results of sediments pollution indices in this study confirmed that the Tigris River is facing probable of environmental pollution especially with dangerous heavy metal such as Cd, which resulted from increased rate of non-treatment industrial waste that are discharged to Tigris River. The geo-accumulation index, contamination factor and pollution load index of Mn that get in present study are agree with previous studies, while the results of Cd exceed the results which recorded in study of Rabee *et al.* (2011) on the Tigris River and study of Rabee *et al.* (2009) on Tigris and Euphrates Rivers.

Table (22): Potential ecological risk index for heavy metals of sediment samples that collected from Tigris River

Stations	E^i_f values	
	Cd	Zn
1	100.8	0.81
2	126	0.78
3	147.9	0.93
4	168	1.08

3.3.2 Assessment of heavy metals pollution in *B. xanthopterus*

3.3.2.1 Bio-accumulation Factor (BAF) and Bio- Sedimentation Factor (BSF)

Bio-accumulation factor (BAF) is the process which causes an increased chemical concentration in an aquatic organism compared to that in water, due to uptake by all exposure routs including dietary absorption, transport across respiratory surfaces and dermal absorption (Mackay and Fraser, 2000). Bioaccumulation can be viewed as a combination of bio-concentration and food uptake. Bio-sedimentation factor (BSF) which is defined as the ratio of the concentration of chemical accumulated inside an organism (from food and direct exposure) to the concentration in sediments. The bio-accumulation

factor (BAF) in fish is the ratio of the concentration of the chemical in the organism to that in the water.

The bio-accumulation of trace metals in fishes includes complex processes, which are controlled by exogenous and endogenous factors. Exogenous factors are reflected to environmental parameters such as metal bioavailability, temperature and alkalinity of ambient aquatic surroundings, whereas endogenous factors include species, age, size, physiological state and type of feeding of fish (Moiseenko and Kudryavtseva, 2001).

The values of bio-accumulation factor and bio-sedimentation factor for fish (*B. xanthopterus*) was shown in Table 23, 24 and 25. The bio-accumulation factor values (BAF) for studied heavy metals in tissues of fish (muscle, intestine and gill) were higher than values of bio-sedimentation factor (BSF).

It was found that the concentration of the studied metals (Cd, Zn, and Mn) in different tissues of fish were several times higher than their concentrations in water. It is obvious from the data given in Table 23, 24 and 25, that the highest values of (BAF) for studied heavy metals were recorded in the gills of the studied fish. However, the lowest values of (BAF) were recorded in the muscles.

The results of this study recorded that the order of BAF values of the studied metals (Cd, Zn, and Mn) in different tissues of fish was as follows: Mn > Cd > Zn and the order of BSF values of the same studied metals in different tissues of fish was as follow: Cd > Mn > Zn.

The BAF values were higher in fish for all studied metals than the concentration in water, which may indicate that the fish had the ability to accumulate metals in their bodies more than the surrounding environment (Javed, 2005). These two factors (BAF) and (BSF) indicate that whether heavy metal bio-magnification takes place through the trophic chain, a value greater than 1 indicate bioaccumulation (Rashed, 2001). The fish can be

considered as a good bio-indicator for cadmium and manganese in Tigris River since, they accumulation in fish with BAF more than 1, while the fish cannot be consider as a bio-indicator for the zinc metal because it had a BAF value lower than 1.

Table (23): The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in muscles *B. xanthopterus* that collected during the study period

Heavy metals	Dissolved average ppm	Sediment average ppm	muscle average ppm	BAF ppm	BSF ppm
Cd	0.004	1.38	0.0043	1.07	0.003
Zn	0.0135	89.84	0.0023	0.17	0.000025
Mn	0.007	232.51	0.03	4.28	0.00012

Table (24): The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in intestine *B. xanthopterus* that collected during the study period

Heavy metals	Dissolved average ppm	Sediment average ppm	Intestine average ppm	BAF ppm	BSF ppm
Cd	0.004	1.42	0.01	2.5	0.007
Zn	0.0135	89.84	0.0023	0.17	0.000025
Mn	0.007	232.51	0.03	4.28	0.00012

Table (25): The bio-accumulation factor (BAF) and bio-sedimentation factor (BSF) of heavy metals in gills *B. xanthopterus* that collected during the study period

Heavy metals	Dissolved average ppm	Sediment average ppm	Gills average ppm	BAF ppm	BSF ppm
Cd	0.004	1.42	0.012	3	0.0084
Zn	0.0135	89.84	0.0026	0.19	0.000028
Mn	0.007	232.51	0.089	12.71	0.00038

Conclusions

It was concluded from the present study that:

1) The trend of studied heavy metals concentrations can be represented as Zn > Mn > Cd for filtered water. While. It was found in sediments as Mn > Zn > Cd, and in fish as Mn > Cd > Zn.
2) Seasonal variations in concentrations of studied heavy metals refer to decrease of these concentrations in winter season, while increase in summer season.
3) In general, the average of heavy metals concentrations for filtered water was within the safe limits of each Iraqi and international standards limits.
4) Tigris sediments in study area were homogenous and prevail by grain of sand, and the concentration of total organic carbon was low.
5) Waters of Tigris River in study area tend to slightly alkaline and with good ventilation, therefore the study area did not record a significant decline in the values of dissolved oxygen to critical levels. Water of Tigris River was classified according to the hardness as hard water.
6) According to correlation coefficients results, the concentrations of studied heavy metals were not affected by fluctuating in physical and chemical properties except electrical conductivity and total dissolved solids that have inverse correlation with above items.
7) Deterioration the water quality of Tigris River was increase towards the downstream of Baghdad city because of pollutants discharge to the river.
8) The results of geo-accumulation index, contamination factor and enrichment factor indices showed that the Cd was recorded high concentrations and exceeded to its background values and may be caused high risk to aquatic environment.
9) Using of pollution load index and contamination degree index to identify of pollution severity by total heavy metals showed that the station 1 and 2

were unpolluted to slightly polluted by studied heavy metals, whereas the station 3 and 4 considered polluted by the same metals.

10) The results of potential ecological risk index indicate a high risk of Cd to the people of Baghdad city.

11) Gills contained the highest concentration of all the detected heavy metals, followed by the intestine, while the muscles tissues appeared to be the least preferred site for bio-accumulation of metals.

12) The bio-accumulation of heavy metals in different tissues of fish was higher than the concentrations of studied heavy metals in water that indicate that the fish has the ability to accumulate metals in their bodies.

Recommendations

It was recommended from the present study that:

1) Restriction of the human, industrial and agricultural discharges to the river.
2) The strict laws should be activated to prevent hazardous pollutants to be higher than standard levels into rivers.
3) Continuous monitoring of concentrations of heavy metals, especially Cd to avoid being overcome permissible limit.
4) Dissemination and increase environmental awareness among the people.
5) Overall, environmental strategies need to be improves to protect and enhance the water quality in Tigris River.

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Table (1): The correlation among cadmium concentrations in water, sediments and fish (muscles, intestine and gills)

Cd				
	Water	**Sediments**	**Muscles**	**Intestine**
Sediments	0.188			
Muscles	-0.106	0.188		
Intestine	-0.229	0.340*	0.239	
Gills	0.012	0.120	-0.029	0.593*

*** Significant at (p<0.05)**

Table (2): The correlation among zinc concentrations in water, sediments and fish (muscles, intestine and gills)

Zn				
	Water	**Sediments**	**Muscles**	**Intestine**
Sediments	-0.342*			
Muscles	-0.338*	-0.127		
Intestine	-0.272*	-0.174	0.750*	
Gills	-0.118	-0.023	0.413*	0.351*

*** Significant at (p<0.05)**

Table (3): The correlation among manganese concentrations in water, sediments and fish (muscles, intestine and gills)

Mn				
	Water	**Sediments**	**Muscles**	**Intestine**
Sediments	0.020			
Muscles	-0.286*	0.052		
Intestine	-0.350*	0.185	0.677*	
Gills	-0.278*	0.378*	0.337*	0.739*

*** Significant at ($p<0.05$)**

الخلاصة

أجريت الدراسه الحالية من اجل التعرف على تراكيز الكادميوم والزنك والمنغنيز في الماء المرشح ورواسب نهر دجلة، وتم قياس نفس المعادن في أنسجة عضلات وامعاء وغلاصم سمك القطان المجموعة من منطقة الدراسة، بالاضافه الى دراسة الخصائص الفيزيائية والكيميائية لمياه النهر. كما قيمت شدة تلوث الرواسب النهريه بالمعادن الثقيلة المدروسة بوساطة استخدام دلائل تلوث الرواسب وهي كل من مؤشر التراكم الارضي (I-geo-Index)، ومؤشر حمل التلوث (PLI-Index)، ومؤشرعامل التلوث (C_f-Index)، ودرجة التلوث (C_d-Index)، ومؤشر عامل الاغناء (EF-Index) ومؤشر الخطر البيئي المحتمل (E^i_f).

وأختيرت اربع محطات في مدينة بغداد تقع على نهر دجلة لغرض أجراء الدراسة. تم أخذ النماذج من هذه المحطات بمعدل مرة واحدة كل شهرين اعتبارا من تشرين الاول لعام ٢٠١١ ولغاية اب ٢٠١٢.

بينت نتائج الدراسه الحالية بأن المعدل السنوي لتراكيز المعادن الثقيله الذائبه (الكادميوم و الزنك والمنغنيز) كان ٠,٠٠٤ و ٠,٠٢٣ و٠,٠٠٧جزء من المليون على التتالي. وأظهرت تراكيز المعادن المدروسة في مياه نهر دجلة تغيرات فصلية خلال فترة الدراسة، وكانت ضمن الحدود المسموح بها من قبل المحددات العراقية لنظام صيانة الأنهار.

أما معدل تراكيز الكادميوم والزنك والمنغنيز في الرواسب فكان ١,٣٨ و ٨٦ و٢٣١,٤ جزء من المليون على التتالي. أظهرت تراكيز المعادن المدروسة في الرواسب تغيرات فصلية معنوية وكانت أعلى مما هي في الماء بشكل كبير.

أما تراكيز المعادن الثقيلة في انسجة عضلات السمك فكان معدلها لكل من الكادميوم والزنك والمنغنيز ٠,٠٠٤٣ و ٠,٠٠٢٣ و٠,٠٣ جزء من المليون على التتالي. بينما بلغ معدل كل من الكادميوم والزنك والمنغنيز في انسجة الامعاء ٠,٠١ و ٠,٠٠٢٣ و ٠,٠٣ جزء من المليون، على التتالي. أما في انسجة الغلاصم فقد كان معدل تراكيزها ٠,٠١٢١ و ٠,٠٠٢٦ و ٠,٠٨٩ جزء من المليون على التتالي.

كما بينت نتائج الدراسة ان تراكيز المعادن المدروسة في انسجة كل من عضلات وامعاء وغلاصم السمك كانت أعلى مما هو في الماء في أغلب الاحيان ولكنها أقل من تراكيزها في الرواسب. وقد أكدت هذه النتائج بقيمة معامل التراكم الاحيائي (BAF) ومعامل الترسيب الاحيائي (BSF).

أما الخصائص الفيزيائية والكيميائية لمياه النهر والمتمثلة في درجة حرارة الهواء والماء والاس الهيدروجني والتوصلية الكهربائية والمواد الصلبه الذائبة والاوكسجين الذائب والمواد الصلبه

العالقة والعسره الكلية فقد سجلت قيما ترواحت ما بين: ١٢-٤٢ مْ و ٩-٣٢ مْ و ٦,٩-٨,٢، و ٤٠٠-٨١٠ مايكروسيمينز و ٢٢٠-٤٥٠ ملغم/لتر و ٥,٦٥- ١٠,٩٧ ملغم/لتر و ٤٥٠-٨٤٤ ملغم/لتر و ٢٠٠-٥٥٠ ملغم/لتر على التوالي.

وفيما يتعلق بتقييم تلوث الرواسب باستخدام المؤشرات البيئية فقد بينت نتائج مؤشر التراكم الارضي (I-geo) المحسوب للعناصر المدروسة أن المحطات المدروسة غير ملوثه بعنصري الزنك والمنغنيز، ولكنها كانت معتدلة التلوث بعنصر الكادميوم، ماعدا المحطه الاولى والتي سجلت تلوثا قليلا بهذا العنصر. كما أظهرت قيم مؤشر حمل التلوث (PLI) بأن كل من المحطه الاولى و الثانيه غير ملوثة بمجموع المعادن المدروسة، بينما المحطه الثالثة والرابعة كانتا ملوثتين بمجموع المعادن المدروسة.

أوضحت نتائج عامل التلوث (C_f) بأن المحطات جميعها سجلت تلوث عاليا بعنصر الكادميوم، ولكنها كانت واطئة التلوث بعنصر الزنك ما عدا المحطه الرابعة، والتي سجلت تلوثا معتدلا بهذا المعدن، بينما سجلت الرواسب تلوثا واطأ بالمنغنيز في كل محطات الدراسة.

وأستنادا الى نتائج مؤشر درجة التلوث (C_d) فقد أعتبرت المحطه الاولى والثانية على درجة واطئه من التلوث بالمعادن المدروسة، بينما كانت المحطات الاخرى معتدلة التلوث. وفضلا عن ذلك فقد بينت نتائج عامل الاغناء (EF) بأن كل المحطات تصنف على انها معتدلة الاغناء بعنصر الزنك، وأغناء مهم ومؤثر بعنصر الكادميوم لكل المحطات ماعدا الرابعه سجلت أغناء عالي جدا.

وأعتمادا على مؤشر الخطوره البيئية المحتملة للمعادن الثقيلة سجل عنصر الكادميوم درجه عاليه نسبيا لاحتمالية الخطوره البيئية في كل من المحطة الاولى والثانية والثالثة، أما المحطه الرابعة فقد سجلت درجه عاليه جدا لاحتمالية الخطوره، بينما قيم نفس المؤشر بينت أن عنصر الزنك لا يشكل خطوره محتملة بالنسبة لكل المحطات المدروسة.

الإهداء

إلى ينبوع الذي لايمل العطاء إلى من حاكت سعادتي بخيوط منسوجه من قلبها إلى حبي الاول والأزل الذي لا ولن يضاهيه اخر، ولا يوفي حقها إلا أسمها ثلاثا أمي، أمي، أمي . . .

إلى من سقى وشقى لأنعم بالراحه والهناء الذي لم يبخل بشيء من أجل دفعي في طريق النجاح أبي العزيز

إلى القلوب الطاهره الرقيقه وإلى من حبهم يجري في عروقي ويلهج بذكرهم فؤادي إخوتي علي وحسين

إلى الارواح التي سكنت تحت تراب الوطن الحبيب الشهداء العظام وأخص بذكر عمي رحمه الله

إلى من سرنا سويا نشق الطريق معا نحو النجاح والأبداع إلى صديقاتي وزميلاتي

هاله مجيد

2013



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بغداد

كليَّة العِلْومِ

تقييم التلوث ببعض العناصر الثقيلة في مياه ورواسب وسمك القطان *Barbus xanthopterus* (Heckel, 1843) في نهر دجله عند مدينة بغداد

رسالة مقدمة إلى
كلية العلوم / جامعة بغداد
وهي جزء من متطلبات نيل درجة الماجستير
في علوم الحياة / علم البيئة

قدمت من قبل

هاله مجيد بلاسم

بكالوريوس في علوم الحياة

جامعة بغداد، كلية العلوم

٢٠١٠

إشراف

أ.د. محمد نافع علي العزاوي   أ.م.د. عادل مشعان ربيع

رجب ١٤٣٤ هـ   أيار ٢٠١٣ م